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AN INVESTIGATION OF PHYSICAL PARAMETERS OF NON-ELECTRICALLY CONDUCTING FINE PARTICULATES

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(Prepared under Contract No. AF 33(616)-8032
by the Houdry Process and Chemical Company, Linwood, Pennsylvania;
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FOREWORD

This report was prepared by the Research Department of the Haudry Process and Chemical Company under USAF Contract No. AF 33 (616)-8032. This project was initiated under Project No. 7350, "Refractory Inorganic Nonmetallic Materials," Task No. 735001, "Refractory Inorganic Nonmetallic Materials: Non-Graphitic." The work was administered under the direction of Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Lt. C. T. Lynch acting as project engineer.

This report covers work conducted from March 1961 to September 1962.

ABSTRACT

The objective of this research is to find one or more measurable properties of active ceramic powders which can be related to sinterability. Samples of active magnesia were prepared by calcination of basic carbonate at 400&900°C. and tested for activity in a closed system. The activity measurements, oxygen exchange and "initial specific adsorption" (of CO_2), indicate that the bulk structure as well as the surface of such materials is extremely active. Both of these tests show that magnesia samples calcined at about 500°C. have higher activity than similar samples calcined at either higher or lower temperatures. There are indications that these measurements can be used to characterize ceramic materials with respect to their sinterability.

Data from decomposition experiments and CO_2 adsorption studies are presented and discussed. These results emphasize the difficulties involved in the preparation of uniform, large-scale lots of activated powders, and the care required in their handling to avoid inadvertent contamination by adsorption of atmospheric constituents (H_2O and CO_2).

This technical documentary report has been reviewed and is approved.

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I. INTRODUCTION

The ability of certain ceramic powders to sinter at relatively low temperatures (1100°-1400°C. for magnesia) is a desirable property in that it permits the formation of strong, extremely pure ceramic bodies. Attainment of strength in high purity ceramics is generally found in conjunction with low porosity (high density) and small grain size in the sintered body.[1]

The fundamental reason that some powders possess this property of sinterability and others do not has not been clearly demonstrated. In a study of sinterable magnesia prepared by calcination of basic magnesium carbonate at Battelle Memorial Institute[2] it was found that, "under the conditions of calcining used, the most sinterable powder was obtained by calcining at 1100°F." (593°C.). The following values for density of sintered compacts (expressed as per cent of theoretical) selected from the Battelle data are typical of the results upon which the above conclusion was based:

Calcination Temperature, °F.	Density of Sintered Compacts* Sintering Temperature, °F. 2000	2300	2600
800	81.0	85.8	89.2
1000	93.3	95.3	97.3
1100	94.3	96.4	97.5
1200	88.3	95.5	97.1
1500	79.1	89.1	96.9

* Density is expressed as per cent of theoretical (MgO = 3.58 g./cc).

This finding of an optimum intermediate calcination temperature was at least partially responsible for initiation of the research project covered by this report. The work at Battelle showed no obvious correlation between sinterability and such properties as surface area, refractive index, volatile content, etc. Therefore, this investigation was started in order to work more directly on the problem of finding some measurable surface or bulk property, possibly more fundamental than had been examined before, which can be used to differentiate between sinterable and unsinterable powders. The contract describes the project as: "A quantitative investigation of the surface and bulk properties related to defective crystal structures and their effect upon sinterability."

In studies of the surface properties of catalysts and catalyst supports various workers in the Houdry laboratories have made measurements interpreted as showing that ceramic surfaces may have severe local strains. These strains give rise to highly energetic, mobile surface atoms which are probably responsible for catalytic activity in certain instances; at elevated temperatures these mobile surface atoms are also considered responsible for sintering.

In this connection, it is interesting to note that in one of these earlier investigations[3] involving measurements of energy of hydration, it was found that

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the maximum hydration energy was observed for samples dehydrated at intermediate temperatures. Similarly, maximum activity for oxygen exchange was shown by samples of oxides treated at intermediate temperatures. When either too low or too high temperatures were employed, the reactivity of the surface was lower.

From these hydration studies it was postulated that: at least a certain energy is necessary to remove the most strongly bonded molecules; the resulting surface is highly strained by the loss of ions from the exterior layer and cooperative forces make the energy of adsorption of the first adsorbed molecules extraordinarily high; treatments carried out at any temperature significantly above that needed for decomposition of the last molecule of progenitor activate the lattice and anneal the high energy sites. The situation at lower temperatures is reversed: only low energy sites lose water; the remaining hydroxyl groups are sufficiently labile to effectively anneal the surface.

It was in the light of this background that the research at Houdry has been directed toward preparing samples of magnesia powder under controlled conditions and attempting to measure some property that would be expected to vary with severity of calcination.

Some experiments on energy of hydration were originally planned; but, in view of the fact that carbon dioxide is retained during the calcination of basic magnesium carbonate (the source of magnesia for this whole project) after most of the water has been evolved, a study of carbonatation (carbon dioxide adsorption) was carried out instead. The essential piece of apparatus for this program was an automatic, recording, thermogravimetric balance with which equilibrium adsorption data were obtained for calculation of isosteric heats. The same apparatus was also used to determine the "initial specific adsorption" of carbon dioxide by magnesia. The values obtained in this latter work are indicative of surface activity, and are shown to correlate with calcination temperature.

The other main area of study involved measurement of oxygen exchange activity. Numerous difficulties were encountered in this work. However, sufficient data were obtained to demonstrate that intermediate calcination temperatures yield powders having maximum exchange activity, and to indicate that this technique of characterizing powders is a valuable tool for further studies in this general area.

In addition to discussions of these two main phases of the research program, the report includes the results of some experiments concerning the decomposition of basic magnesium carbonate and properties of the resultant magnesia powders.

This is a final summary report for the period from 15 March 1961 through 14 September 1962.

II. EXPERIMENTAL

MATERIALS

1. Basic Magnesium Carbonate

Mallinkrodt Chemical Company's A. R. Grade basic magnesium carbonate was used throughout this project for the preparation of samples of magnesia by thermal decomposition. It was selected because it had been used extensively in the work at Battelle and because it is reputed to be consistent in quality and low in impurities. The approximate formula printed on the label, $4\ MgCO_3 \cdot Mg(OH)_2 \cdot 4\ H_2O$, indicates a theoretical magnesium oxide content of 43.1% for this material.

2. Nitrogen

A pre-purified grade of nitrogen, supplied by Air Reduction Company, was used as the purge gas in all experiments involving the thermogravimetric balance. It was found to be essentially free of oxygen and low in moisture content (dew point $<-68°C.$).

3. Carbon Dioxide

Carbon dioxide adsorption studies were made with 100% Coleman grade carbon dioxide purchased from the Matheson Company. For some experiments, prepared mixtures of the same grade of carbon dioxide and pre-purified nitrogen were obtained from the same company. Traces of oxygen were removed by passing the gas through a cobaltous oxide deoxidizing tower. The dew point of the pure carbon dioxide was $<-68°C.$

4. Water Enriched with Oxygen^{18}

For most of the oxygen isotope exchange experiments a supply of water enriched with oxygen^{18} which had been purchased from the Stuart Oxygen Company before this project was undertaken was used. According to the label, the isotopic enrichment of this material was 1.4 atom per cent. However, because the results of most of the recent analyses were closer to 1.5% this value has been used in calculating oxygen exchange activity.

Two other lots of enriched water were purchased in order to obtain a supply having approximately 5% enrichment. It was felt that use of the more highly enriched material would improve the accuracy of the results. The first of these more concentrated lots, purchased from the Isomet Corporation, could not be used because it also contained far greater than normal quantities of deuterium which so complicated the mass spectrometer results that they were completely meaningless. Toward the end of the report period a second lot of water of approximately 5% enrichment, normalized to the natural abundance of deuterium, was obtained from YEDA Research and Development Company of Israel. Although it arrived too late to be of much use in the exchange experiments, it was through the use of this material that the effects of adsorption on the mass spectrometer results were recognized. In turn, this led

to the development and adoption of the standard analytical procedure for oxygen^{18} in water by the mass spectrometer (see Appendix II).

APPARATUS

1. Thermogravimetric Balance

A photograph of the thermogravimetric balance assembly, used for both decomposition and adsorption experiments, is shown in Figure 1. This apparatus features an Ainsworth, Model AV-AU-2, automatic, recording, analytical balance. The balance is mounted on a three-legged steel table above a vertical tube furnace. Samples, suspended in the furnace from the balance, are heated to temperatures as high as 900° C. The furnace platform support can be raised and lowered to facilitate charging and discharging samples.

The furnace controls are mounted on a panel just below the recorder. The main heating circuit can be controlled automatically at a pre-selected temperature level, but temperature changes at controlled rates must be made manually. Likewise, the separate heating circuits at each end of the furnace are controlled manually in order to maintain isothermal conditions in the sample zone of the furnace. Three thermocouples, located at different levels in the furnace and connected to the recorder through a timer, provide a constant record of furnace temperatures. The heating mantle, which may be seen in Figure 1 directly above the furnace, was installed to minimize convection currents in the weighing chamber.

A McDanel combustion tube, with Pyrex glass connections sealed on at each end, is used in the high temperature section of the weighing chamber. Connection through a mercury seal to another section of Pyrex glass attached to the bottom of the balance base plate completes the gas-tight weighing chamber. The counterbalance, glass beads in a glass container, is suspended from the right balance pan in an unheated glass chamber. This enclosed system is especially suitable for experiments involving weight changes in controlled atmospheres.

Auxiliary equipment, not shown in Figure 1, consists of pressure reducers, gages, tubing, valves, rotameters, etc. needed for bringing the gases into and out of the apparatus. Purge gas introduced at the bottom of the furnace, flows upward through a quartz chip preheat section, past the sample holder, and out the side-arm gas exit tube above the furnace to a vent system. In addition, a seal gas stream of pure nitrogen, introduced through another side-arm tube just above the gas exit tube, protects the balance mechanism from the volatile products of decomposition carried away from the sample by the purge gas.

Figure 2 is a photograph of two types of sample holder that may be used in conjunction with the thermogravimetric balance. Both hold about the same amount of sample. It is obvious that the one on the left, a porous alundum crucible, confines the sample more than the one on the right, and limits contact between the sample and the purge gas. The other one, called the tier-tray sample holder, consists of a series of twelve shallow Vycor glass trays, placed one above another on

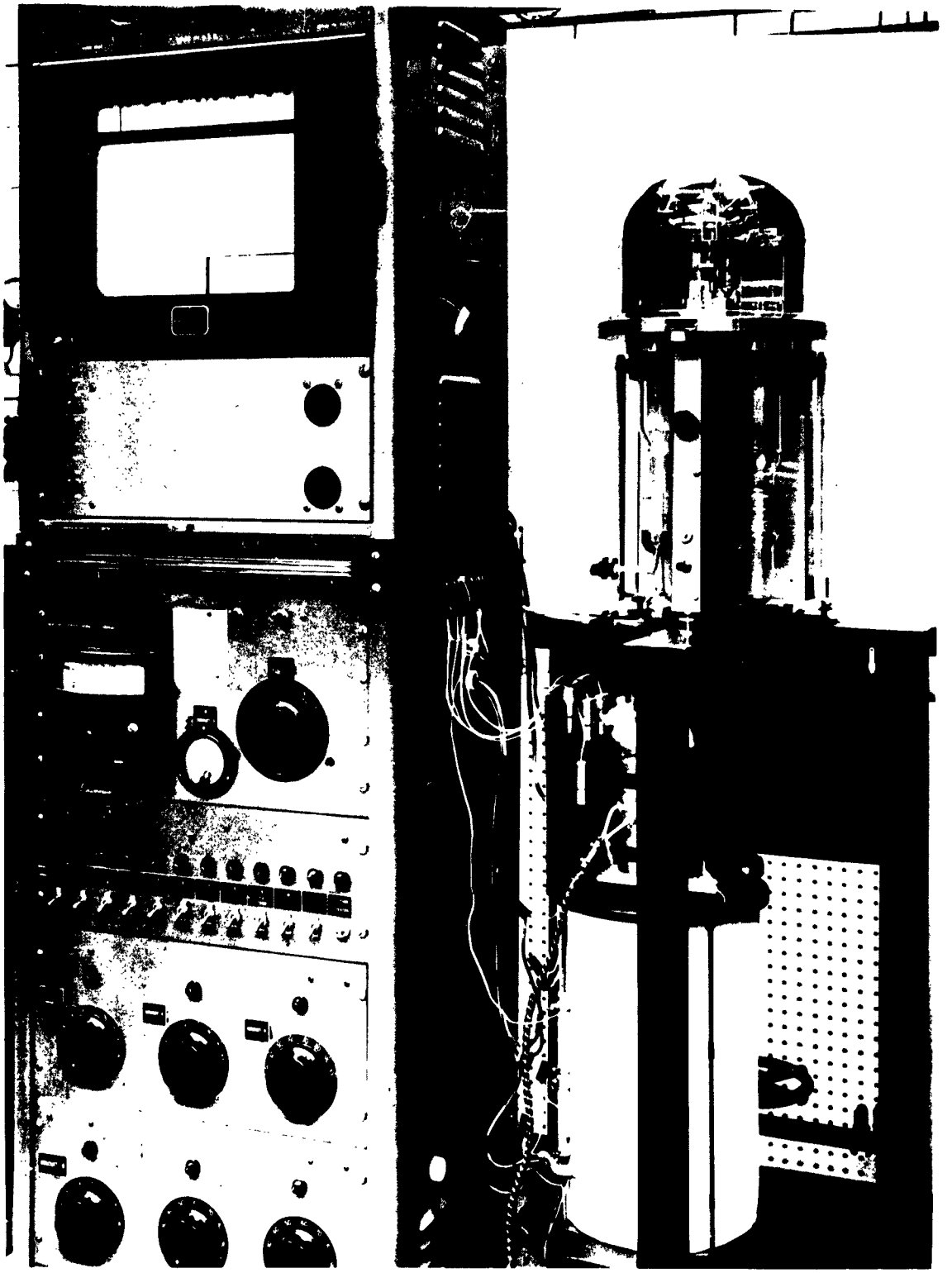


FIGURE 1 THERMOGRAVIMETRIC APPARATUS

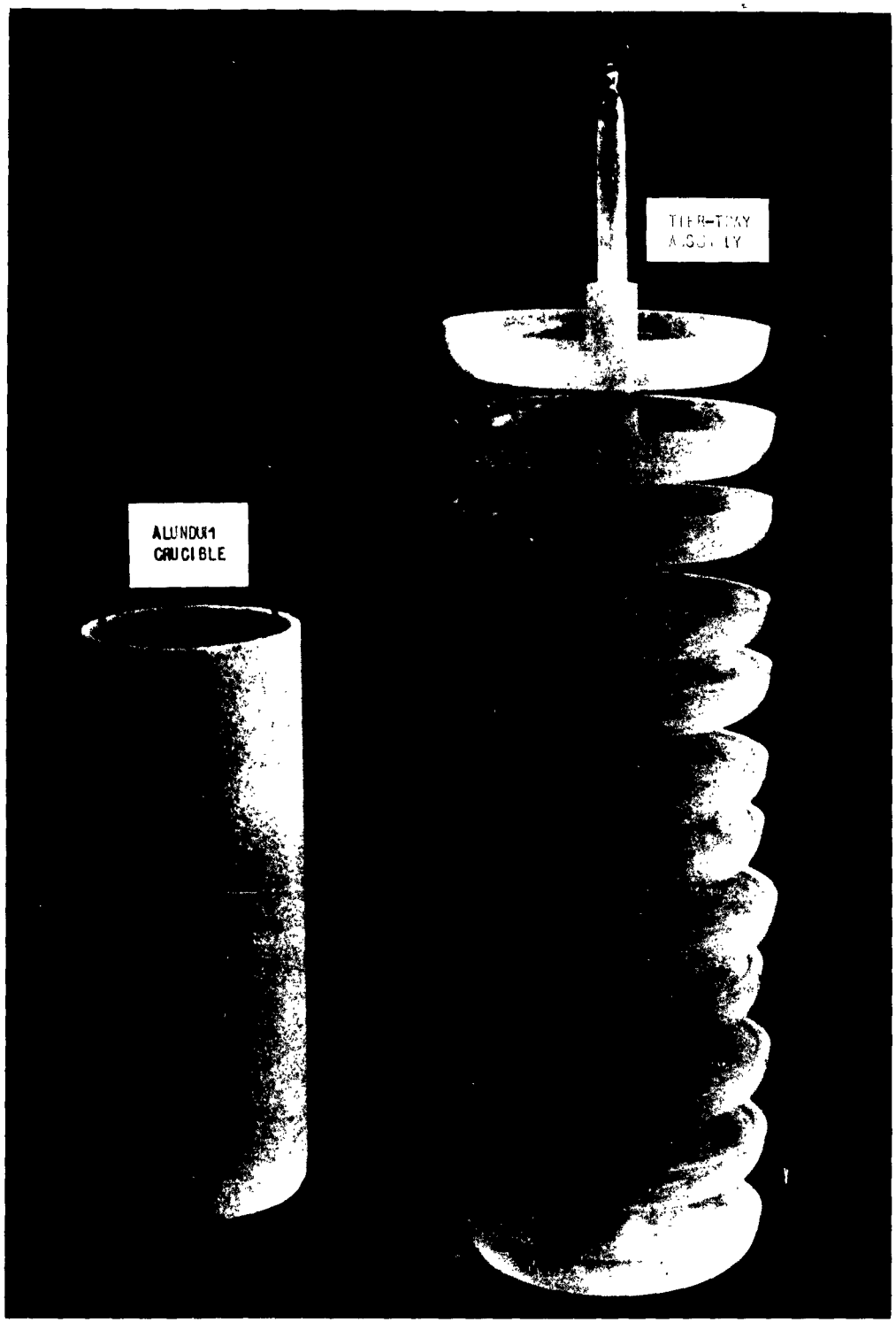


FIGURE 2 SAMPLE HOLDERS FOR THERMOGRAVIMETRIC APPARATUS

a Vycor rod. With this arrangement the decomposition products released on heating a sample are quickly swept away by the purge gas stream because the sample is well exposed. For the same reason this sample holder is especially suitable for adsorption studies. The alundum crucible sample holder was used only once--to demonstrate the change in rate of decomposition of basic magnesium carbonate caused by confinement of the sample during heating.

Another tier-tray assembly, made up of stainless steel trays, was used briefly for carbon dioxide adsorption experiments, but had to be abandoned when it was found that the trays oxidized appreciably under the conditions of these particular experiments.

2. Oxygen Exchange Apparatus

Initially, plans for studying surface properties of magnesia by means of oxygen isotope exchange experiments were based on the use of an apparatus in which changes in the concentration of H_2O^{18} were to be monitored continuously by thermal conductivity measurements. The apparatus was designed and built, but it was not used for exchange experiments because calibration runs showed it to lack the sensitivity needed to detect the small changes in concentration that would be expected in this investigation.

Other ideas were tried and discarded before a workable system was developed. The essential feature of this new apparatus is a specially designed reactor assembly which is shown in Figure 3. The oxygen^{18} enriched water for each experiment is charged into a small glass break-tube by means of the assembly pictured in Figure 4 which permits the water to be weighed accurately. The sketch of the complete apparatus in Figure 5 shows where these two pieces are attached to the main vacuum system. Items not shown in Figure 5 include a temperature recorder and automatic temperature programmer and controller (1000°C. maximum) for use with the calcining furnace, and a thermostated water bath for controlling the temperature of the reactor during the exchange reaction.

EXPERIMENTAL TECHNIQUES AND PROCEDURES

1. Decomposition Experiments

Several experiments were made with the thermogravimetric balance to obtain information about the decomposition of basic magnesium carbonate and/or to prepare samples of magnesia (by calcination of the basic carbonate at different temperatures) for surface area measurement. These experiments were similar in that decomposition of the sample was accomplished by raising the furnace temperature at a rate of 100°C. per hour. This rate of heating was usually maintained until the maximum temperature was reached. In certain instances, however, the rate was increased several fold after the temperature passed 500°C. Since decomposition is nearly complete at this temperature, changes in heating rate above 500°C. should have little or no effect on the properties of the residual magnesia. Products of decomposition were carried away

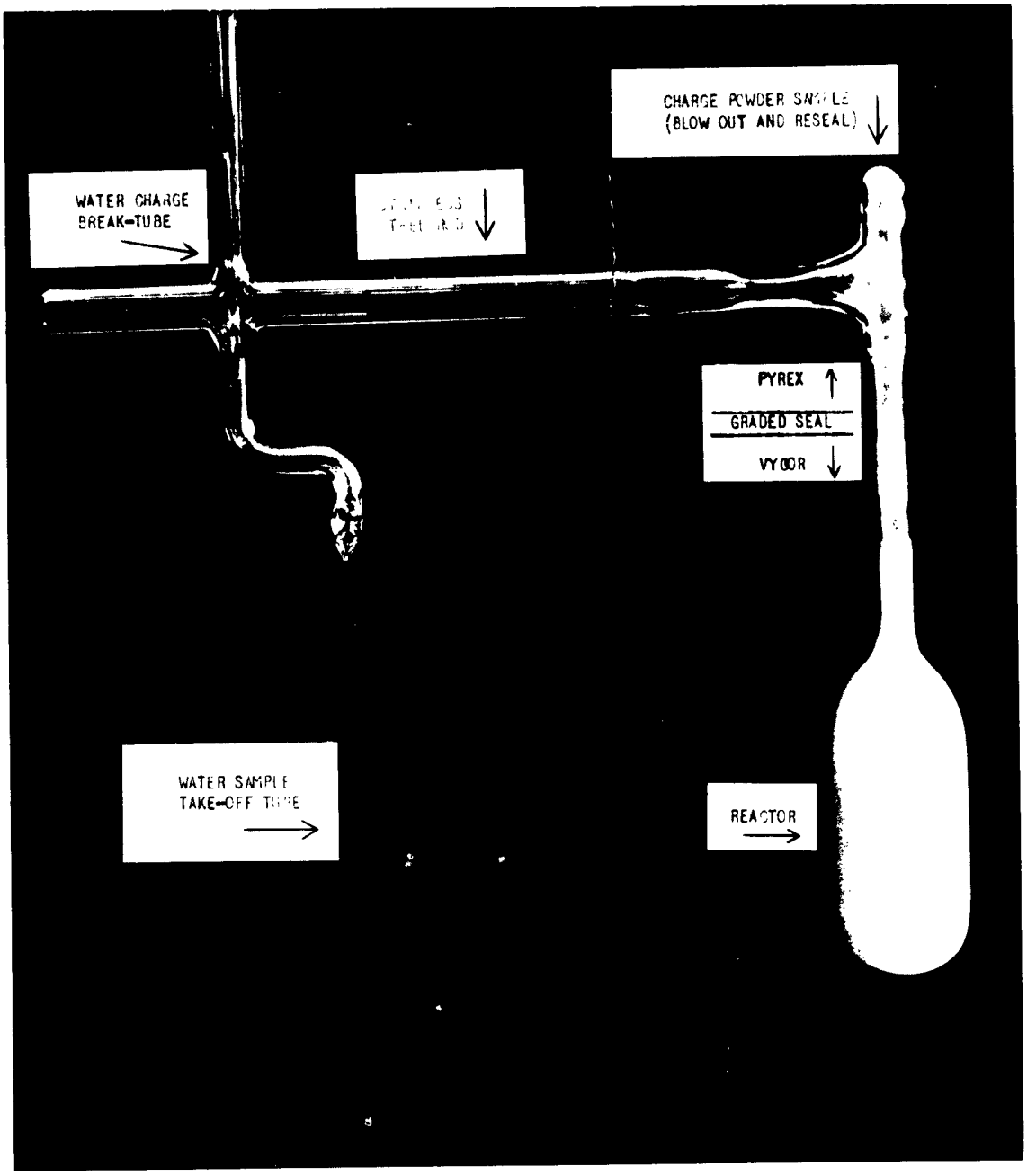


FIGURE 3 REACTOR ASSEMBLY FOR OXYGEN EXCHANGE APPARATUS

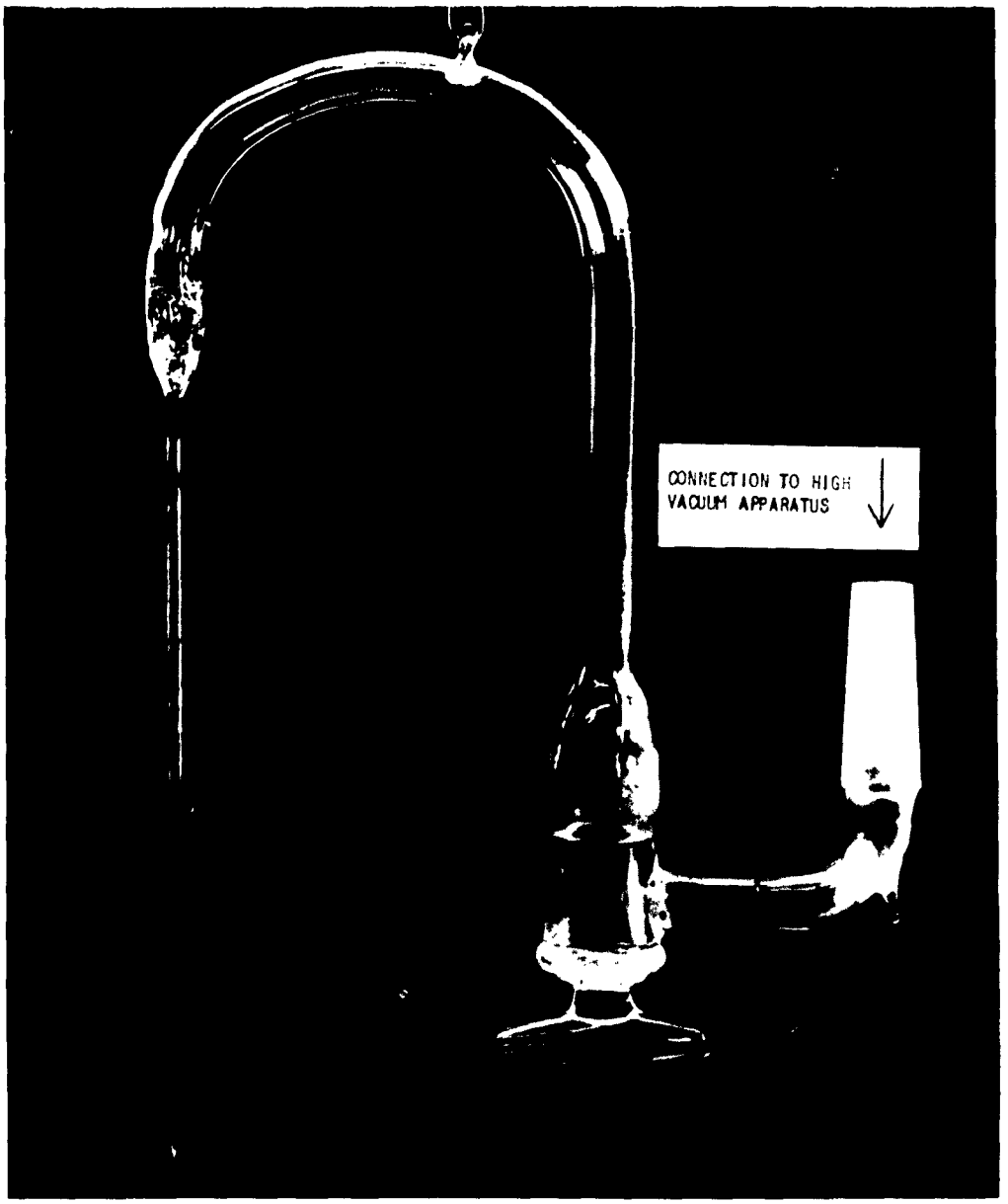


FIGURE 4 TUBE FOR CHARGING AND WEIGHING ISOTOPICALLY ENRICHED WATER

A- EXPANSION BULB
B- ENRICHED WATER SUPPLY
C- TUBE FOR CHARGING AND WEIGHING ENRICHED WATER
E- GAS BURETTE
F- CONSTANT VOLUME MANOMETER
G- REACTOR ASSEMBLY
H- FURNACE
I- CONNECTIONS TO PROGRAMMER CONTROLLER
J- HIGH VACUUM SOURCE
K- MC CLEOD GAGE

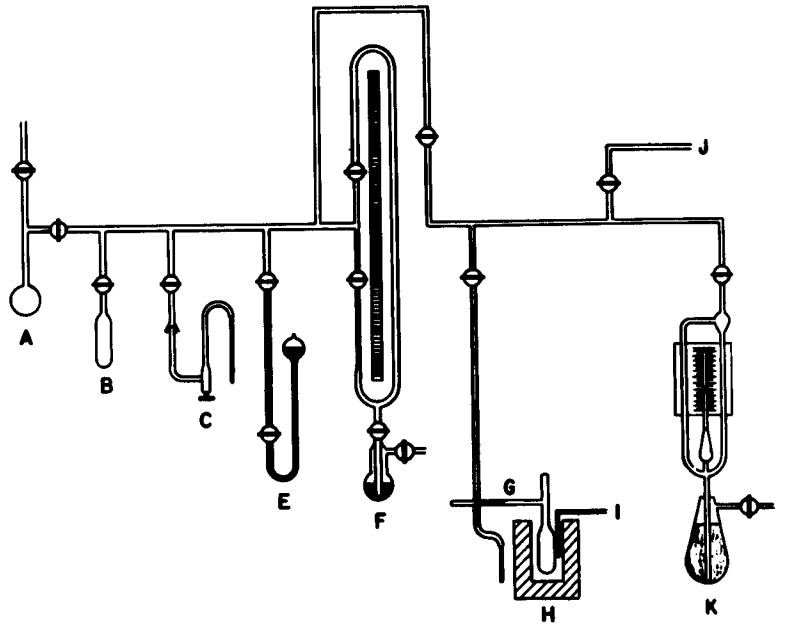


FIGURE 5 OXYGEN EXCHANGE APPARATUS

by nitrogen flowing through the furnace at 250 cc/minute. At this rate the atmosphere around the sample was changed at least once a minute.

Surface areas of the magnesium oxide powder samples resulting from calcination of the basic carbonate were measured by the BET method using nitrogen as the adsorbate. Precautions were taken to prevent unnecessary exposure of the samples to the atmosphere during their transfer to the surface area apparatus in order to avoid excessive adsorption of carbon dioxide or water vapor.

2. Equilibrium Adsorption Experiments

This second type of experiment carried out with the thermogravimetric balance involved the same technique for preparing magnesia samples described in the preceding section. The finished samples were then treated at various temperatures, while still in the apparatus, with pure carbon dioxide or mixtures of carbon dioxide and nitrogen of known composition. The use of purchased blends of carbon dioxide and nitrogen (1% and 8.4% CO_2) was an important factor in achieving consistent results. By metering one or the other of these blends into the system with a metered stream of pure nitrogen, mixtures having intermediate concentrations were obtained.

This group of experiments includes those in which adsorption of carbon dioxide was allowed to proceed at various controlled conditions until the sample weight reached equilibrium. In general, a sample was considered to have reached equilibrium when its change in weight was 0.01% or less per hour. This same criterion was used in preparing magnesia samples by thermal decomposition to judge when the reaction had stopped.

Results of these experiments are discussed in the Appendix.

3. Dynamic Adsorption Experiments

The dynamic adsorption experiments are those in which samples of magnesia, prepared in the thermogravimetric balance by thermal decomposition of basic magnesium carbonate, were contacted in situ with flowing, pure carbon dioxide at one of two adsorption temperatures, 400° or 200° C., one of which is well above the decomposition temperature of magnesium carbonate and one below it. The chart drive of the balance recorder was operated at high speed during these runs to obtain accurate measurements of carbon dioxide adsorption during the first few minutes of contacting. All samples were treated with carbon dioxide for 100 minutes after which they were cooled without further purging, removed from the furnace, and the surface area measured.

The preparation of samples for these studies differed slightly from the technique used in the two preceding series of experiments; the rate of heating the powder to decomposition temperature was 300°/hour rather than 100°/hour. Thus it was possible to reach any desired calcination temperature in a reasonable time without changing the rate of heating. This heating rate was not considered to be excessive for use with the tier-tray sample holder because of the high degree of exposure it affords the material being heated.

4. Blank Runs

In order to obtain meaningful data with the thermogravimetric balance, certain corrections must be applied to the observed weights. The following factors affect the apparent weight of the sample:

a. gas flow

b. furnace temperature

c. gas composition

The effect of each of these factors was investigated by making a blank run in which the empty sample holder was weighed at various temperatures in air, nitrogen, and carbon dioxide. All weighings were made both with gas flowing at the standard rate of 250 cc/minute and with no gas flow. With correction charts developed from these results it was possible to convert the observed sample weights, measured in flowing gas (air, nitrogen, carbon dioxide, or mixtures of two of these gases) at temperatures up to 900°C., to the values that would be obtained in static nitrogen at room temperature. These corrections were used in conjunction with the experiments involving decomposition and equilibrium adsorption.

The dynamic adsorption experiments required a somewhat different type of correction chart for use only under very specific conditions. This was obtained by making a blank run in which the sample trays contained inert material, similar to magnesia in density. With the system at equilibrium in static nitrogen at temperature (400°C. or 200°C.), and with the recorder chart running at top speed, a 250 cc/minute flow of carbon dioxide was started through the furnace and continued until the apparent weight equilibrated at a lower value (due to the greater buoyancy of carbon dioxide). By utilizing data from this blank run in dynamic adsorption experiments, it was possible to make appropriate buoyancy corrections to the values obtained very soon after the introduction of carbon dioxide (while the weighing chamber contained a mixture of nitrogen and carbon dioxide of changing concentration). At both temperatures equilibrium was reached quite rapidly: 48 seconds after the start of carbon dioxide flow at 400°C. and 84 seconds at 200°C.

5. Oxygen Exchange Experiments

In testing for oxygen exchange activity, a weighed sample of basic magnesium carbonate and a sealed break-tube containing a weighed quantity of air-free water enriched with oxygen-18 were charged to the reactor assembly (Figure 3) which was then sealed onto the high vacuum apparatus (Figure 5). This same vacuum apparatus was used to charge the enriched water to the break-tubes by allowing it to expand from the supply tube into an evacuated bulb and then condensing and freezing the water in the break-tube with liquid nitrogen.

With the reactor assembly attached to the vacuum apparatus and the furnace in position around the sample contained within the Vycor bulb section, the furnace temperature was raised at a constant rate (8-9°C./minute) to a pre-selected calcination temperature. By holding the reactor at calcination temperature for approximately 18 hours with continuous pumping the pressure within the system was usually reduced to 1×10^{-5} mm, or less. (At calcination temperatures below 400°C. a longer pumping time was required.)

The reactor assembly containing enriched water in a sealed break-tube and the sample of magnesia which had been prepared under vacuum, was sealed, removed from the vacuum apparatus, cooled, and placed in a thermostated water bath maintained at the proper temperature for the oxygen exchange reaction (100° or 50°C.). When equilibrium conditions had been established in the water bath the reactor assembly was removed momentarily, just long enough to break the small tube containing the enriched water, and then replaced in the bath. The reaction time could be controlled quite closely because it started when the water charge tube within the assembly was broken and ended when the water sample collection tube was immersed in liquid nitrogen to freeze out the water vapor in the system.

The water sample, sealed in the collection tube, was removed from the reactor assembly and analyzed for H_2O^{18} content by means of the mass spectrometer.

III. RESULTS AND DISCUSSION

THERMAL DECOMPOSITION OF BASIC MAGNESIUM CARBONATE

In the preparation of sinterable magnesia powders from basic magnesium carbonate by thermal decomposition (calcination), relatively large quantities of volatile compounds (water vapor and carbon dioxide) are evolved. Calculations based on the formula, $4\ MgCO_3 \cdot Mg(OH)_2 \cdot 4\ H_2O$, indicate the composition of the starting product to be:

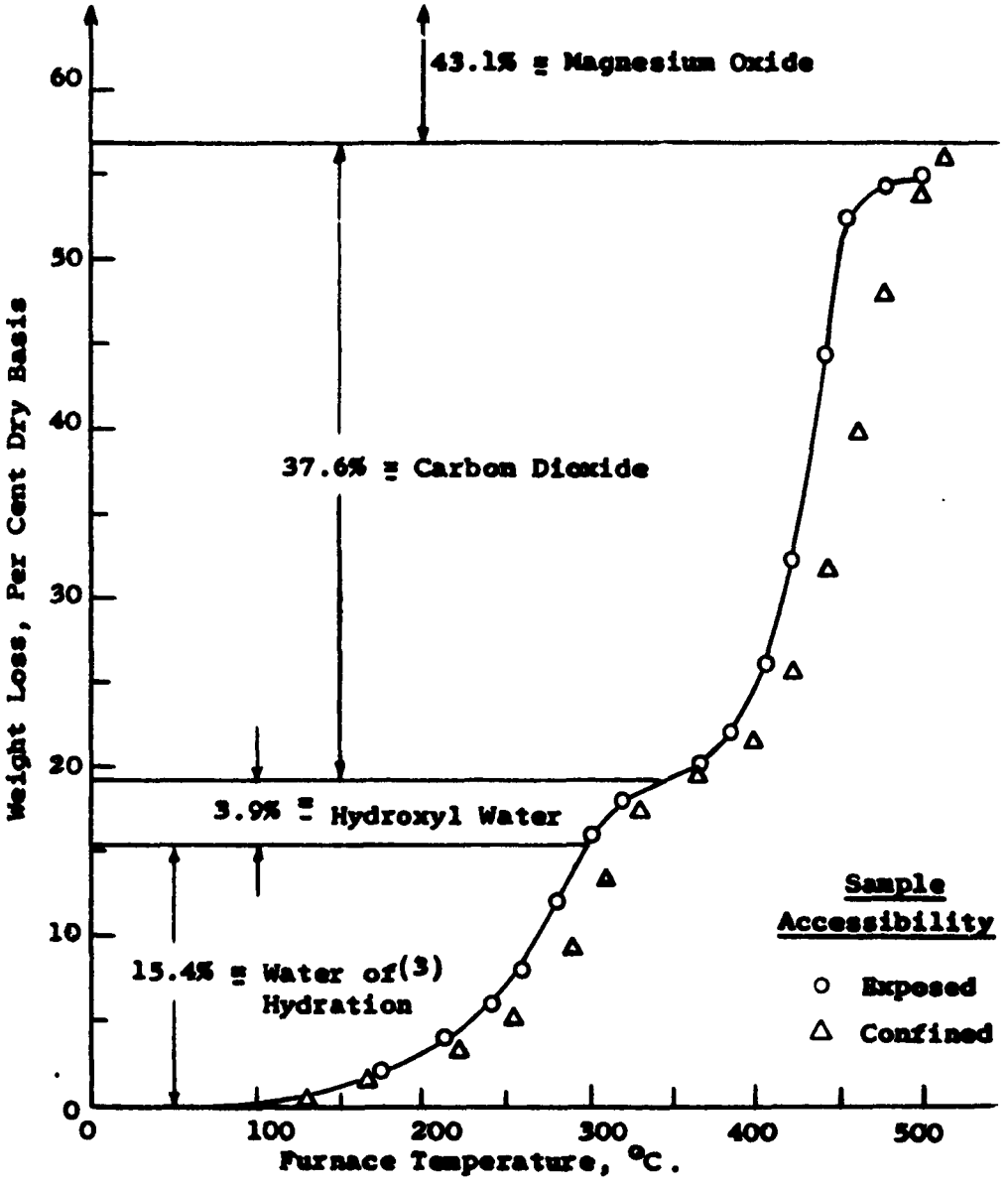
Water of Hydration	15.4%
Hydroxyl Water	3.9
Total Water	19.3
Carbon Dioxide	37.6
Total Volatiles	56.9
Magnesium Oxide	43.1

Three main factors which affect the evolution of volatile components during calcination are (1) calcination temperature, (2) time at calcination temperature, and (3) rate of heating to calcination temperature. Even when these variables are held constant, rates of decomposition may be influenced appreciably by the atmosphere surrounding the sample. At one extreme, the decomposition might take place in the presence of carbon dioxide and water vapor, perhaps under pressure. Under these conditions decomposition would proceed appreciably slower than it would in dry air or inert gas, particularly if done at reduced pressure.

The highest rates of decomposition would be expected at conditions under which the products of decomposition are carried away as soon as they are formed. This can be accomplished by purging the system continuously with a relatively large volume of dry, inert gas or by an efficient vacuum system. Maximum decomposition rates will, of course, not be attained if the products of decomposition cannot escape freely, due to confinement of the sample within a container.

The effect of sample container design on the rate of decomposition of basic magnesium carbonate was investigated briefly. Thermal decomposition data were obtained in which the only variable was the degree of confinement of the sample, dictated by the shape of the container. The two sample holders used, a porous alundum crucible for the confined sample and a series of shallow Vycor trays for the exposed sample, are pictured in Figure 2.

The decomposition curve for the exposed sample is shown in Figure 6. Decomposition data for the confined sample are plotted on the same graph, but are not connected by a line. It is clear that, even though a relatively low heating rate was maintained, the exposed sample lost weight at an appreciably faster rate than did the confined sample. Between 350° and 375°C. the two sets of data almost coincide because of a sharp drop in the rate of decomposition in this temperature range. However, as the rate increases above 375°C. the curves diverge even more. Equilibration



NOTES:

1. Assumed formula of dry charge: 4 $MgCO_3$ $Mg(OH)_2$ $4H_2O$.
2. Furnace temperature raised 100°/Hr. to 500°C., then equilibrated at 515°C.
3. Evolution of volatile components is not confined within the illustrative boundary lines.

FIGURE 6 THERMAL DECOMPOSITION OF BASIC MAGNESIUM CARBONATE

of the exposed sample at 515°C. was achieved with 8 hours additional heating, whereas the confined sample required 20 hours. The 515°C. equilibrium weight loss values for the two runs, 56.1% and 56.0%, are within the limits of experimental error.

The above results emphasize the difficulties that can be expected in calcining a large quantity of the basic carbonate by ordinary techniques, such as heating a large container full of powder in an oven or a muffle furnace. Even under ideal conditions of temperature control and efficient purging of the atmosphere in the heating chamber the effect of the container would be at least as great as, and probably much greater than, was observed here where the amount of powder decomposed was only five grams.

It is apparent that very special technique is required in order to achieve reproducible results in the preparation of significant amounts of any ceramic oxide powder by calcination of a compound which gives off appreciable quantities of volatile matter during decomposition. Development of a satisfactory means of preparing usable quantities of ceramic powders is considered essential to any investigation in which samples are to be prepared for sintering experiments.

In these experiments and others involving the preparation of magnesia by decomposition of the basic carbonate in the thermogravimetric balance apparatus the carbonate powder was always equilibrated in flowing nitrogen at room temperature to remove adsorbed vapors before it was heated. The thermal decomposition data cited above were based on the weight of this "dry" material, the composition of which was assumed to correspond to the formula: $4\ MgCO_3 \cdot Mg(OH)_2 \cdot 4\ H_2O$. This assumption was supported by further heating a sample to 900°C. The total weight loss at that temperature was 56.9%, as expected from the formula. Thus, throughout this project it has been assumed that the amount of magnesium oxide (900°C. ignited basis) available from a sample of basic carbonate can be estimated quite accurately by multiplying the equilibrium "dry" (room temperature) weight by 0.431.

An idealized graphical representation of the theoretical composition of basic magnesium carbonate is included in Figure 6 with the decomposition data. It is intended to show the relative proportions of the various volatile components. It should not be taken to mean that these components are evolved within sharply defined temperature zones. It has been determined that water is the chief decomposition product at low temperatures. Above 300°C. the rate of carbon dioxide evolution increases sharply while the rate of water loss declines. It is thought that at least part of the hydroxyl water is held quite strongly by the magnesia and not given off below 500°C.

In Figure 7 the residual volatile content of various samples of calcined magnesia is related to temperature of calcination. In all instances the non-volatile content (MgO) was calculated from the equilibrium weight at room temperature, as described above. This correlation was particularly useful in calculating the results of the oxygen exchange experiments.

Most samples of magnesia prepared in the thermal balance were subjected to some treatment that might be expected to affect surface area. However, three

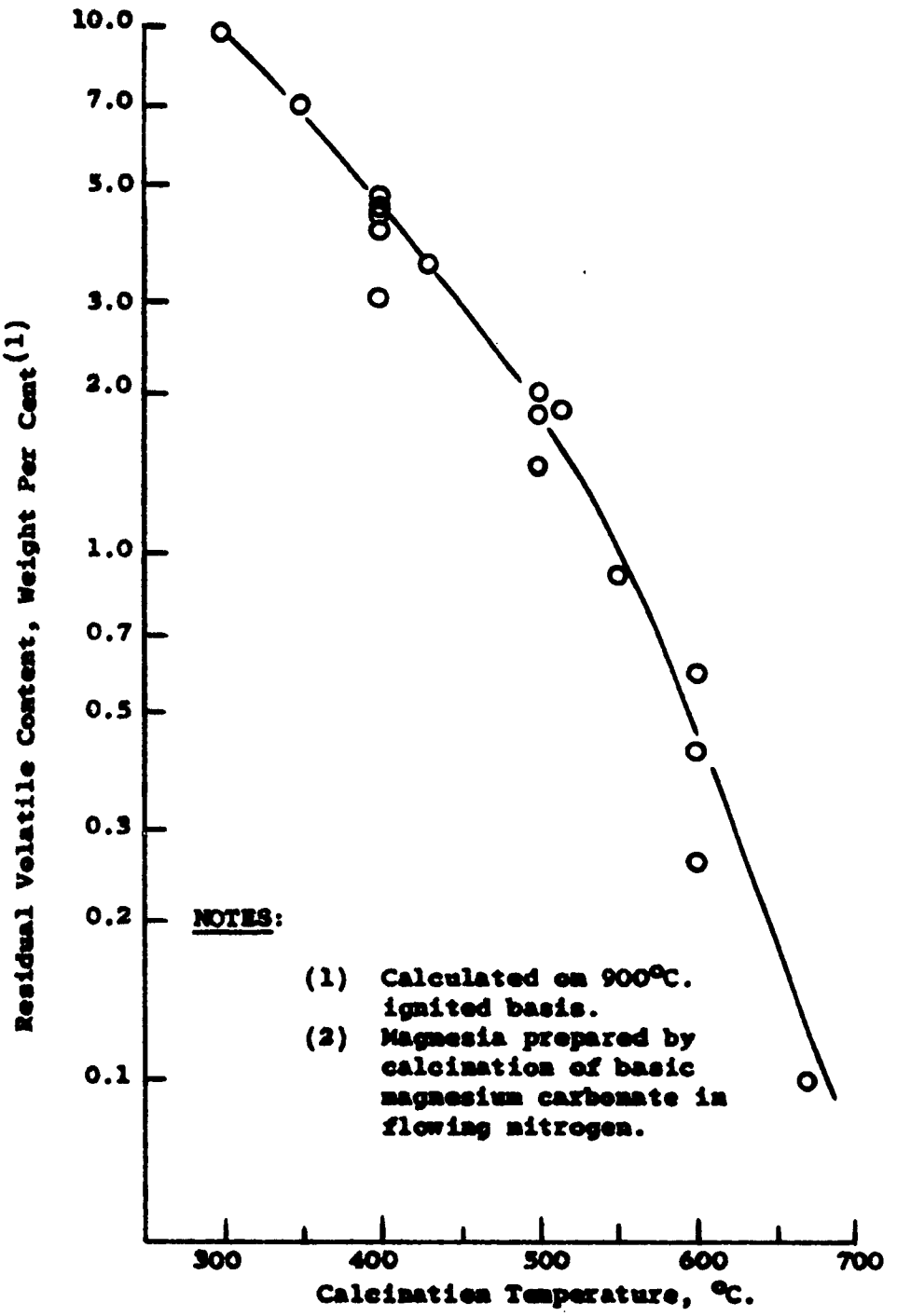


FIGURE 7 RESIDUAL VOLATILE CONTENT OF MAGNESIA(2)

preparations were made primarily for surface area measurement. Results of these tests are as follows:

Calcination Temperature, °C.	Surface Area, $m^2/g.$
400	278
600	94
900	58

The above values were used in drawing the curve in Figure 8 to provide an approximate correlation of surface area with calcination temperature over the range 400°-900°C. Other data shown in this Figure are discussed in the section on dynamic adsorption experiments.

DYNAMIC ADSORPTION OF CARBON DIOXIDE

"Initial specific adsorption" is an arbitrary term to express the results of the dynamic adsorption experiments in terms of surface activity. Samples of magnesia, prepared at different calcination temperatures, were treated with pure carbon dioxide as described under Experimental Techniques and Procedures. An "initial specific adsorption" value for each preparation was calculated from the weight of carbon dioxide adsorbed during the first ten minutes, the weight of the sample at the start of adsorption, and the surface area of the discharged sample. These values are considered to be indicative of surface activity. The amount adsorbed in these experiments was less than that necessary to form a monolayer of carbon dioxide on the surface of the magnesium oxide (0.25 mg CO_2/m^2).

Values for "initial specific adsorption", determined at two different adsorption temperatures (400° and 200°C.), are plotted as a function of calcination temperature in Figure 9. At both temperatures the curves indicate maximum activity for samples calcined at about 500°C.

At the end of each of the dynamic adsorption runs the powder sample was discharged and tested for surface area. This information was needed for calculating the "initial specific adsorption." A comparison of these surface area results with those for samples which had not been contacted with carbon dioxide is found in Figure 8. Here it is seen that values for samples which were treated with carbon dioxide at 400°C. fall on or very near the original correlation curve whereas the data for samples treated at 200°C. are generally below the curve. No special significance can be attached to these low values at this time.

Knowledge of the rates at which carbon dioxide is adsorbed by freshly calcined magnesia powders is important in considering how to handle sizable quantities of such powders to minimize, or completely eliminate, inadvertent contamination of the product with adsorbed vapors. Results of the dynamic adsorption experiments are presented as amount adsorbed as a function of time in Figures 10 through 13. The curves demonstrate clearly that active magnesia has the capacity to adsorb appreciable

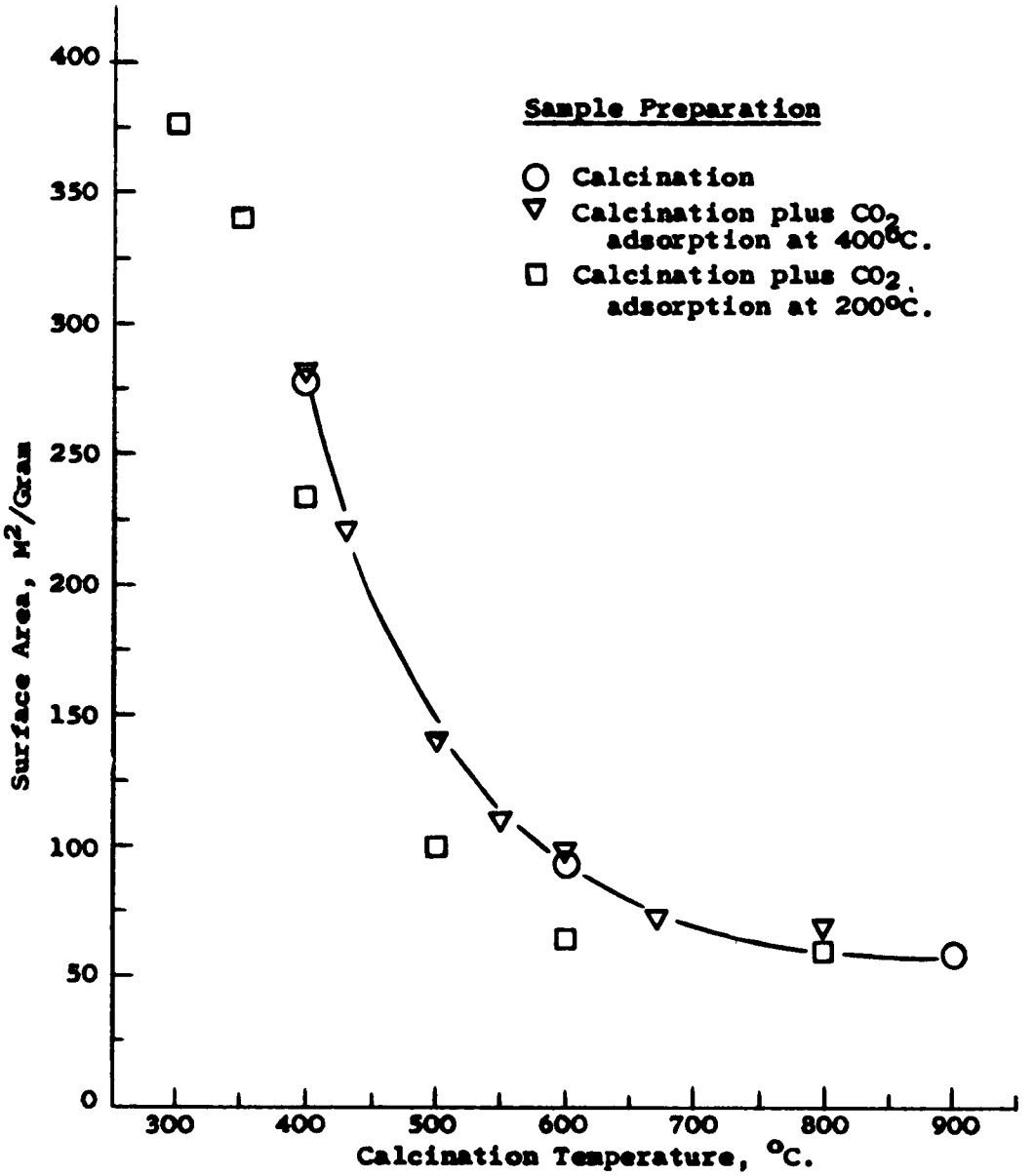


FIGURE 8 SURFACE AREA OF MAGNESIA

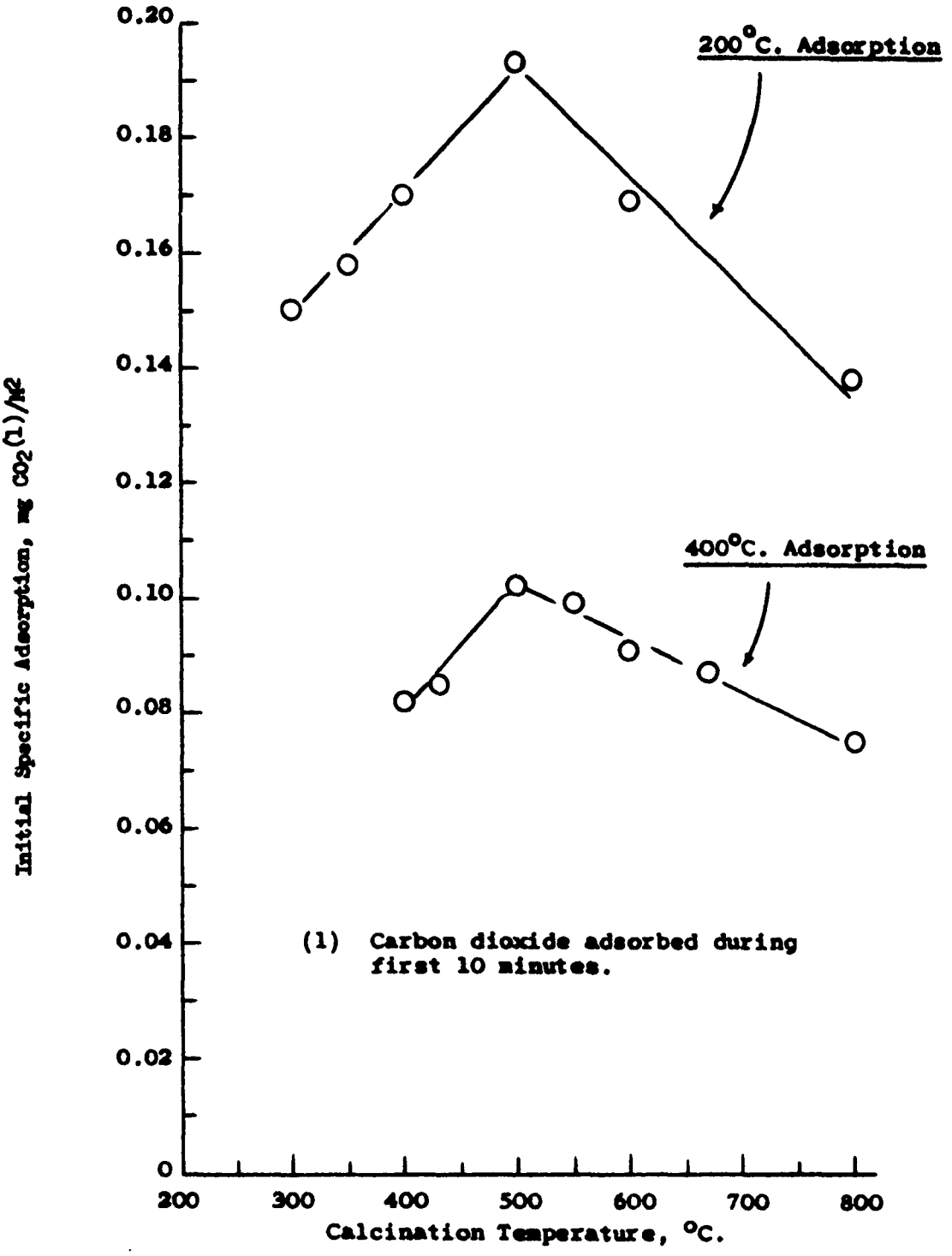
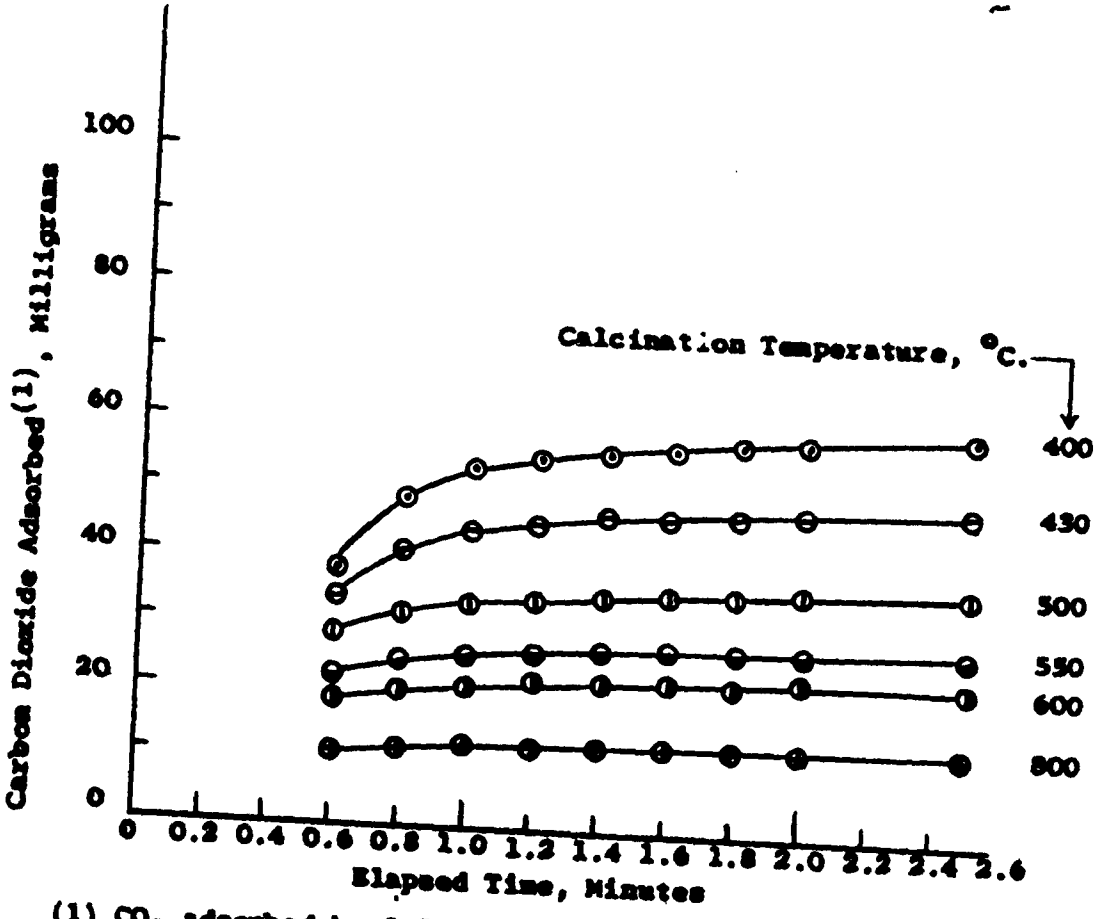
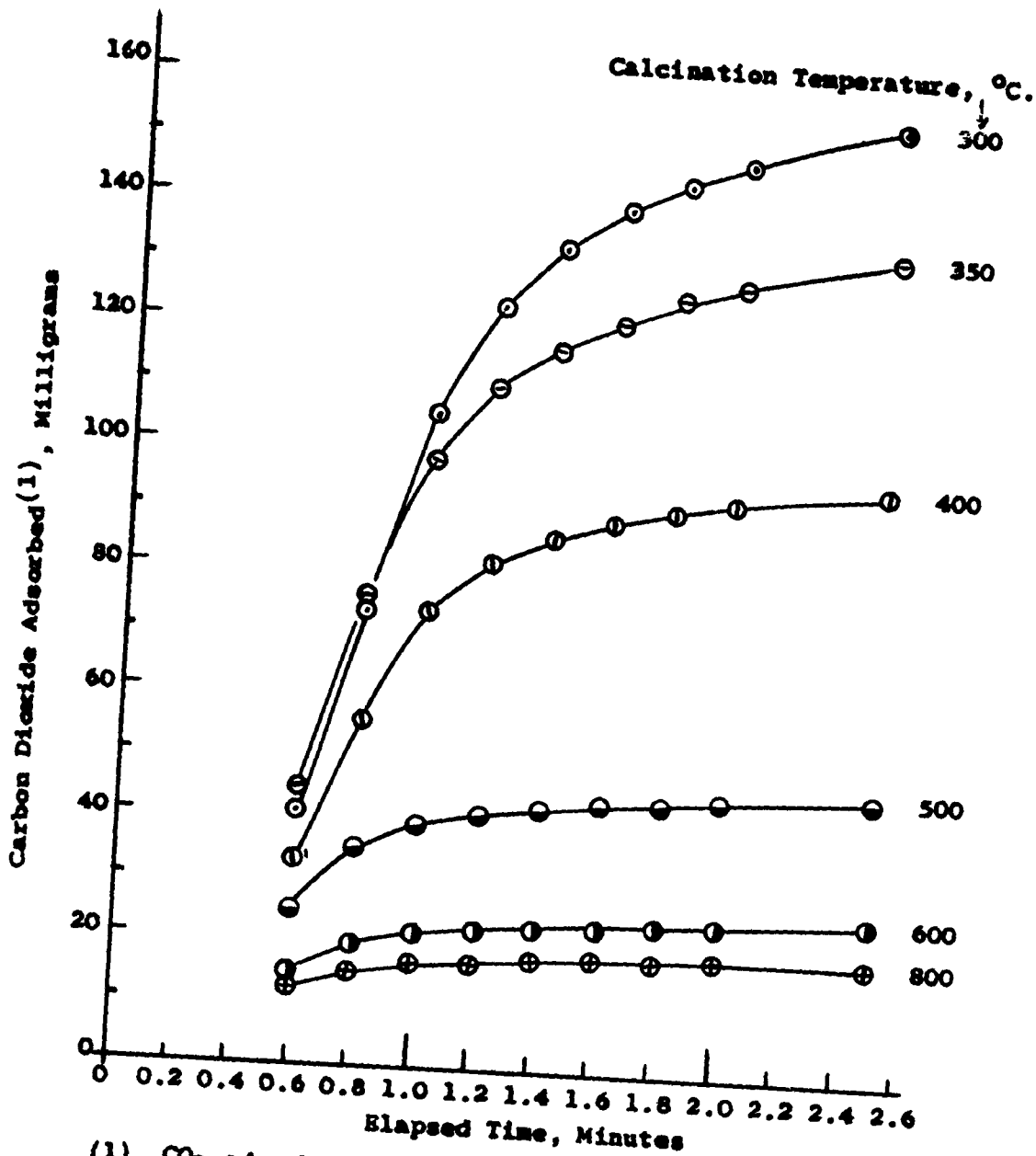


FIGURE 9 INITIAL SPECIFIC ADSORPTION OF CARBON DIOXIDE BY MAGNESIA



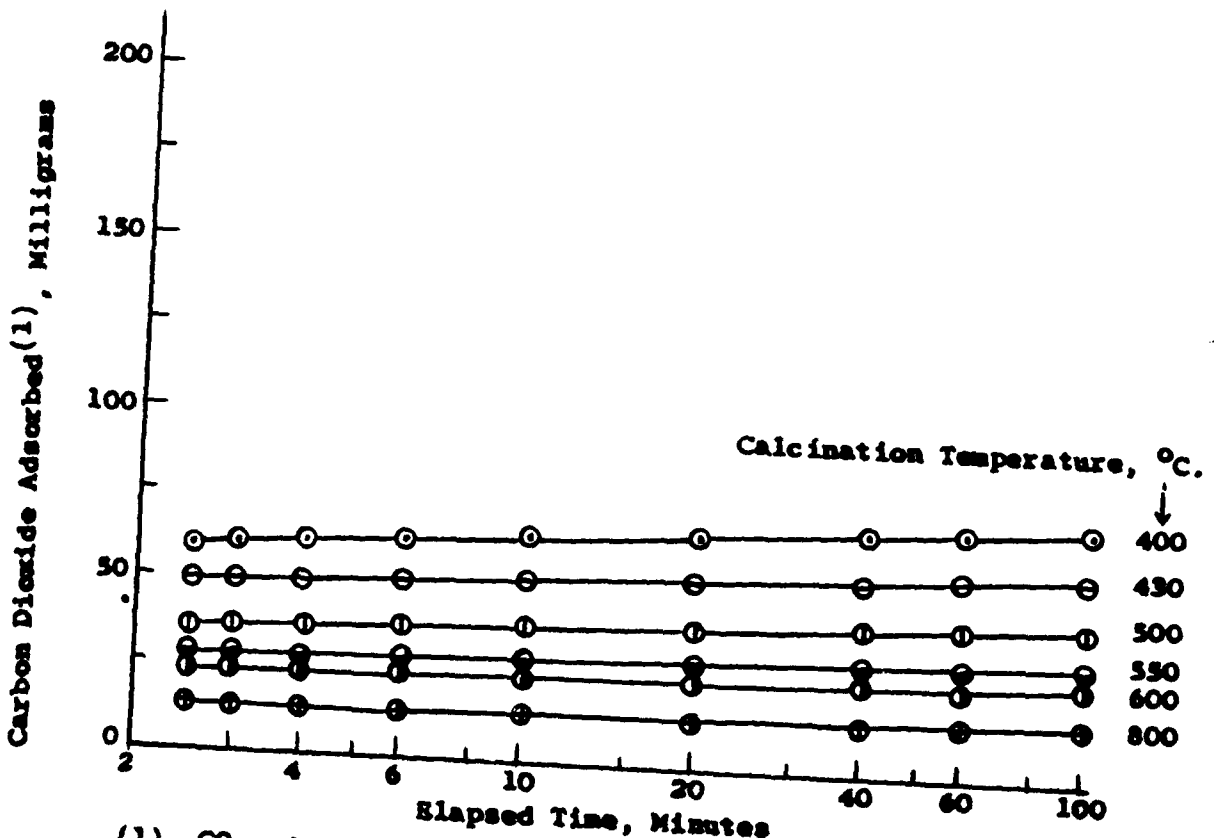
(1) CO_2 adsorbed by 2.7 grams of activated magnesia.

FIGURE 10 INITIAL ADSORPTION OF CARBON DIOXIDE BY MAGNESIA AT 400°C.



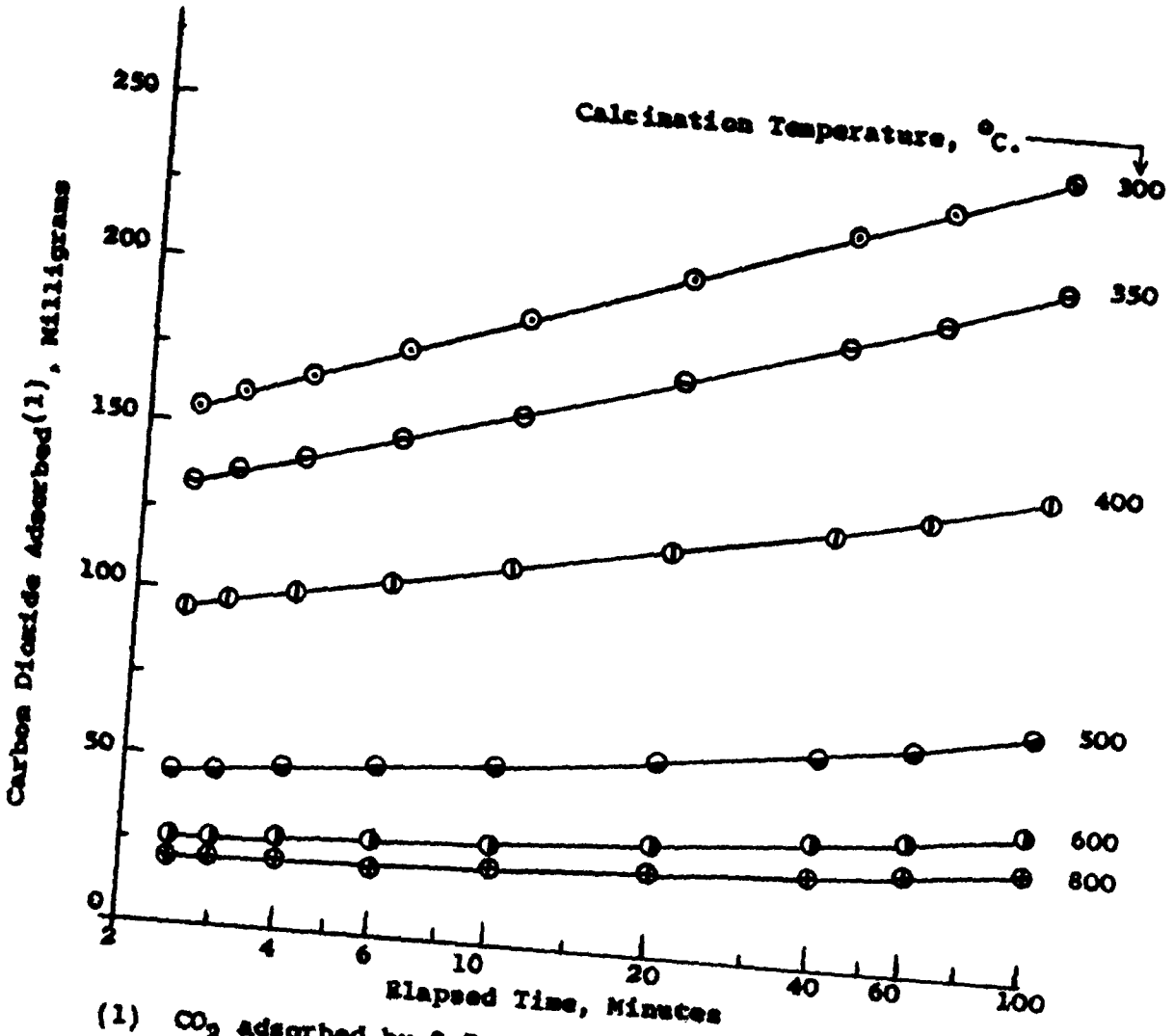
(1) CO_2 adsorbed by 2.7 grams of activated magnesia.

FIGURE 11 INITIAL ADSORPTION OF CARBON DIOXIDE BY MAGNESIA AT 200°C.



(1) CO_2 adsorbed by 2.7 grams of activated magnesia.

FIGURE 12 CONTINUED ADSORPTION OF CARBON DIOXIDE BY MAGNESIA AT 400°C.



(1) CO_2 adsorbed by 2.7 grams of activated magnesia.

FIGURE 13 CONTINUED ADSORPTION OF CARBON DIOXIDE BY MAGNESIA AT 200°C.

quantities of carbon dioxide in a very short time. Similar behavior would be expected in the presence of water vapor or a mixture of carbon dioxide and water vapor such as that normally found in the atmosphere.

The results of an isolated experiment demonstrate what can happen with respect to adsorption of carbon dioxide by magnesia under more normal circumstances. A sample of reagent grade magnesium oxide was taken directly from the stock bottle. Three portions were analyzed for carbon dioxide after different treatments. The analyses were:

Sample Treatment	CO_2 Content, %
None	0.73
Ignited at 900°C.	0.05
Exposed to air for 3 days	1.78

These figures show that, despite the relatively low concentration of carbon dioxide in the atmosphere, exposure of activated magnesia to air must be avoided if high purity is desired.

OXYGEN EXCHANGE BETWEEN MAGNESIA AND WATER

Oxygen exchange has been widely used as a measure of reactivity of various oxide materials, particularly catalysts. Thus it was natural to employ this technique in characterizing magnesia.

The values obtained for exchange activity at 100°C. for samples of magnesia calcined at various temperatures (350°-900°C.) are plotted in Figure 14. Similar data for activity at 50°C. are shown in Figure 15, and both sets of experimental results are listed in Table I. The plots of data in Figures 14 and 15 show the per cent of equilibrium exchange attained at three different reaction times as a function of calcination temperature. These results clearly indicate that the samples having maximum exchange activity are those which were calcined at 500° or 550°C.

Figures 14 and 15 also show that, under the conditions of this test, oxygen exchange activity is appreciably higher at 50°C. than at 100°C. At the former temperature the most active materials achieved the maximum exchange level in 30 minutes. At 100°C. the same degree of exchange required about 60 minutes. These rate differences are shown more clearly in Figure 16 where the exchange activity values for all samples calcined at 550°C. are plotted as a function of time. The anomalous trend of these results, higher activity at a lower temperature, is thought to be due to the eight-fold difference in the vapor pressure of water at the two reaction temperatures. It is possible that a change in amount of water charged or in the size of the reaction chamber could compensate for this difference. However, the main significance of these experiments lies in their demonstration of a maximum in exchange activity for magnesia samples calcined at 500°-550°C. The fact that this trend was observed at two distinct sets of reaction conditions provides additional evidence of the existence of an optimum calcination temperature.

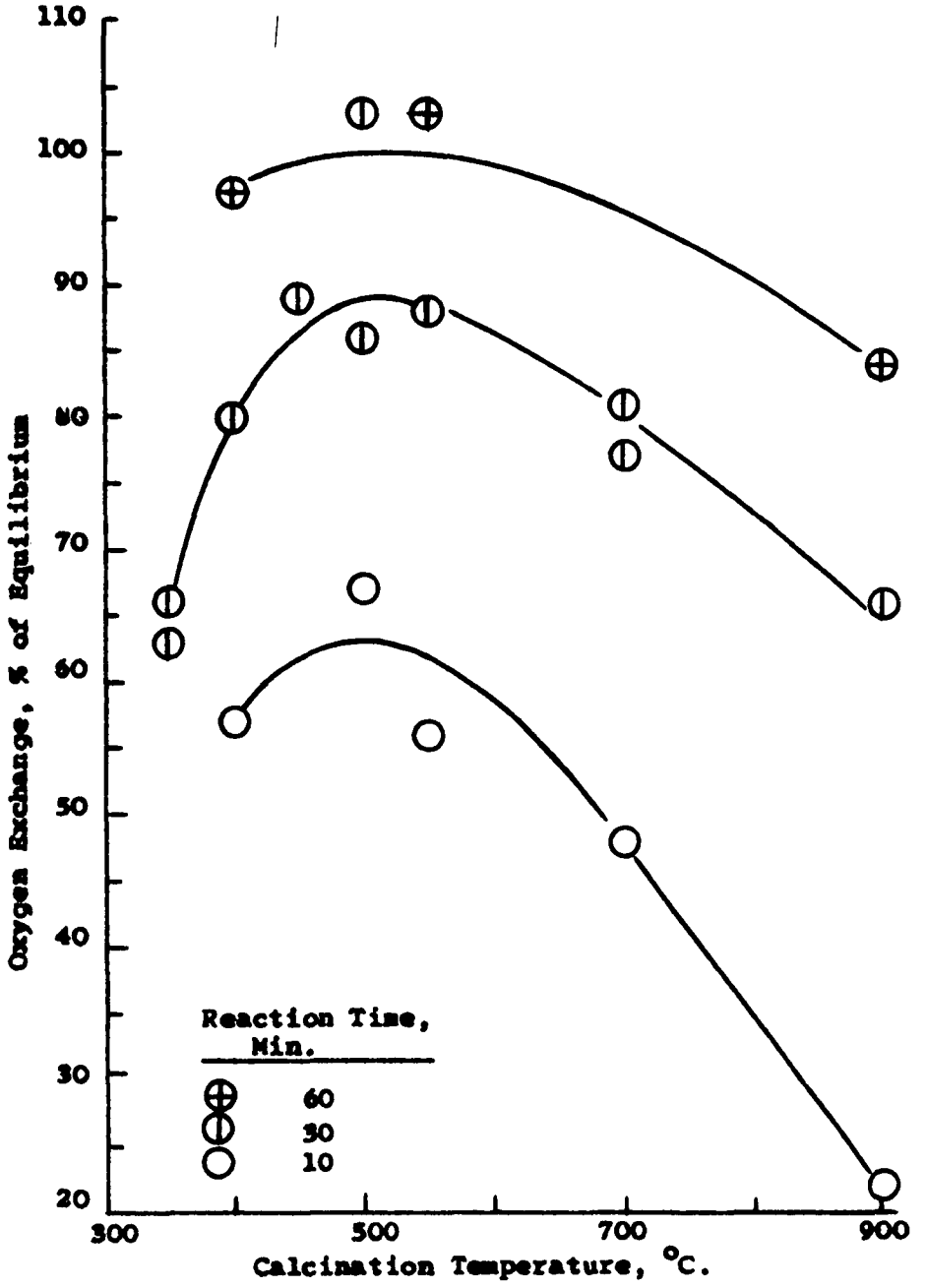


FIGURE 14 OXYGEN EXCHANGE BETWEEN MAGNESIA AND WATER AT 100°C.

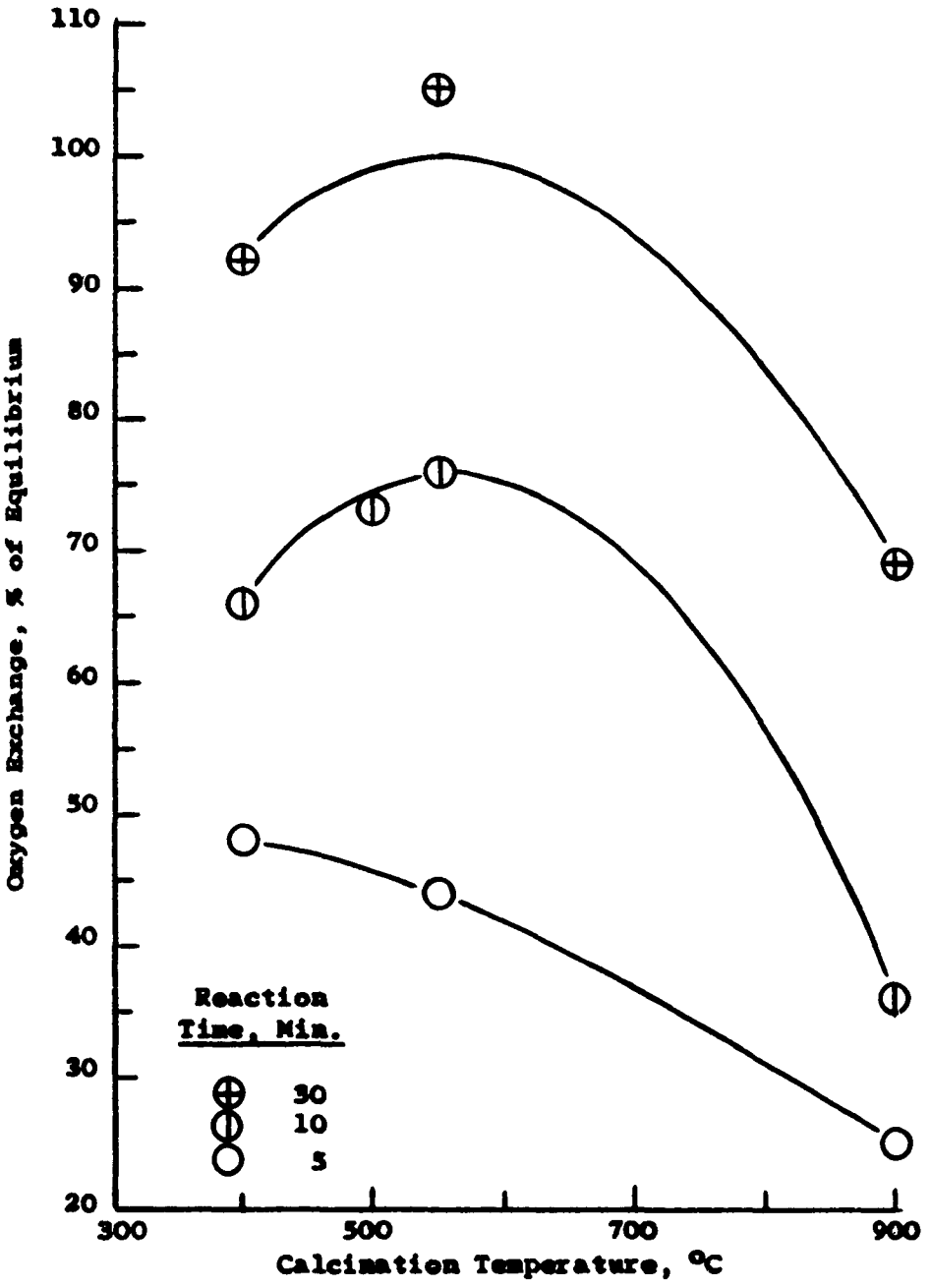


FIGURE 15 OXYGEN EXCHANGE BETWEEN MAGNESIA AND WATER AT 50°C.

Table I

Oxygen Exchange Between Magnesia and Water

MgO Calcination Temperature, °C.	Reaction Temperature, °C.	Reaction Time, Minutes	Oxygen Exchange, % of Equilibrium
350	100	30	63,66
400	100	10	57
400	100	30	80
400	100	60	97
450	100	30	89
500	100	10	67
500	100	30	103,86
550	100	10	56
550	100	30	88
550	100	60	103
700	100	10	48
700	100	30	77,81
900	100	10	22
900	100	30	66
900	100	60	84
400	50	5	48
400	50	10	66
400	50	30	92
500	50	10	73
550	50	5	44
550	50	10	76
550	50	30	105
900	50	5	25
900	50	10	36
900	50	30	69

Notes: 1. Water enriched with 1.5 atom per cent oxygen^{18} was used to permit measurement of oxygen exchange.

2. Magnesia was prepared by calcination of basic magnesium carbonate under vacuum.

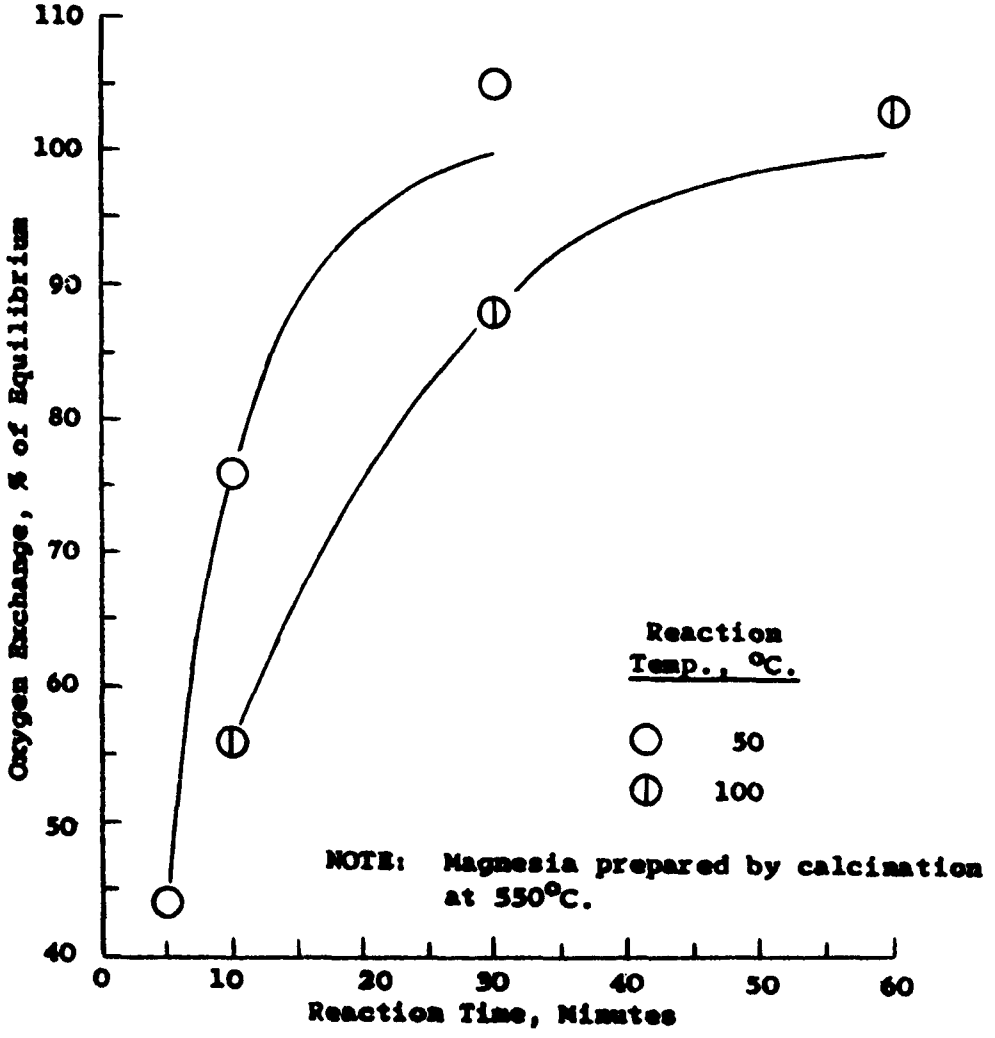


FIGURE 16 RATE OF OXYGEN EXCHANGE BETWEEN MAGNESIA AND WATER

It is evident that the curve for five minute reaction periods at 50°C. (Figure 15) differs from the other curves in that it does not reach its maximum at an intermediate temperature. This may be due to a limitation of the test. The advisability of attempting such short reaction periods with this technique is questionable. In general, the results for the entire series of experiments are quite consistent. Two of the three check runs are in good agreement. Development of a suitable technique for handling the isotope-enriched water samples in the mass spectrometer was essential in bringing the test to its present state of precision. A description of the analytical technique is included in the Appendix.

GENERAL DISCUSSION

Surface energy is generally thought to be related to sintering. Although no sintering experiments were included in this investigation, the finding of maximum activity for magnesia samples calcined at an intermediate temperature range (500-550°C.) is consistent with the results of sintering studies made at Battelle Memorial Institute.[2] It was pointed out in the Introduction that the Battelle investigators reported maximum sinterability for magnesia powders resulting from the calcination of basic magnesium carbonate at an intermediate temperature (approximately 600°C.). The fact that the optimum calcination temperature range determined by the Houdry investigation is somewhat lower than that found at Battelle is consistent with the preceding discussion of the effect of sample confinement on rate of decomposition.

The two types of activity test described in this report indicate essentially the same optimum calcination temperature, despite marked differences in the techniques of sample preparation. Oxygen exchange tests were made with samples obtained by calcining only 0.1 gram of the basic magnesium carbonate, with continuous evacuation, whereas approximately 6.5 grams of powder was decomposed in flowing nitrogen at atmospheric pressure for each of the dynamic adsorption tests.

Also, although results of both tests provide a measure of reactivity, the "initial specific adsorption" values are thought to be indicative of surface activity only. The oxygen exchange data, however, reflect a high degree of activity for the entire (bulk) structure. In the first instance, results are based on the amount of carbon dioxide adsorbed during the first ten minutes of a reaction that requires several hours to reach equilibrium. Therefore, these test results are representative of surface activity. By contrast, the oxygen exchange reaction reaches or approaches equilibrium in an hour or less, depending on test conditions. Thus, it is a measure of bulk activity.

Although there are indications that the activity tests discussed in this report are relatable to sinterability, it should be emphasized that the samples were prepared and tested in situ. Thus, the obvious difficulties involved in preventing atmospheric contamination of activated powders did not have to be considered. In any extension of this program involving large scale powder preparations and sintering experiments, control of atmospheric contamination will be one of the major problems.

IV. CONCLUSIONS

(1) The rate of thermal decomposition of basic magnesium carbonate in a continuously purged system is influenced appreciably by the degree of exposure of the sample during heating.

(2) The surface areas and residual volatile contents of magnesia powders derived from the thermal decomposition of basic magnesium carbonate decline sharply with increasing calcination temperature.

(3) Maximum surface activity, as measured by "initial specific adsorption" of carbon dioxide, is exhibited by magnesia powders resulting from the calcination of basic carbonate at approximately 500°C.

(4) Activated magnesia powders, when contacted with carbon dioxide, exhibit a high rate of adsorption for two or three minutes, then continue to adsorb at a steadily decreasing rate over a relatively long period. The amount of carbon dioxide adsorbed during a given period varies inversely with adsorption temperature and with calcination temperature.

(5) Maximum total activity, as measured by oxygen exchange between magnesia powder and water, is exhibited by magnesia samples derived from calcination of basic magnesium carbonate at about 500°C.

V. RECOMMENDATIONS

It is recommended that this program be continued and extended to include the following areas of investigation:

1. Other preparation variables
2. Different starting materials
3. Hydrogen-deuterium exchange activity
4. Other oxide systems.

The ultimate goal of the research should be to directly relate at least some of the measurements of surface activity to sinterability. This will necessitate the preparation of appreciably larger samples of active powders on which, both surface activity and sintering data can be obtained. Major problems are anticipated in achieving uniform decomposition, in minimizing contamination by adsorption, and in studying the sinterability of compacts prepared from these samples under closely controlled conditions.

APPENDIX I

EQUILIBRIUM ADSORPTION EXPERIMENTS

Results from the first of the equilibrium adsorption experiments are presented graphically in Figure 17 in which variations in the volatile content of a single sample of activated magnesia, after equilibration in nitrogen or carbon dioxide, are plotted as a function of the number of calcinations in nitrogen at 500°C. The following statements are based on information resulting from this experiment:

1. The capacity of activated magnesia to adsorb carbon dioxide increases sharply with decreasing temperature of adsorption.

2. Carbon dioxide adsorbed at 500°C. or lower on a sample of magnesia originally calcined at 500°C. cannot be removed in a reasonable time by purging with nitrogen at temperatures below 500°C. It is removable at 500°C., with purging.

3. An activated magnesia powder prepared by 500°C. calcination gained weight when cooled to a lower temperature in flowing nitrogen. The amount of weight gained varied directly with the temperature difference. This weight increase is thought to be caused by traces of moisture in the nitrogen.

4. The capacity of a single sample of activated magnesia to adsorb carbon dioxide decreases with repeated calcinations at 500°C., thus indicating loss of surface area. An actual sample, calcined nine times at 500°C., had a surface area of 103 m^2/g. According to the correlation in Figure 8, it would have had 145-150 m^2/g. surface area after a single calcination.

In another equilibrium adsorption experiment carbon dioxide isotherms were determined with a sample of magnesia that had been calcined at 400°C. In Figure 18 the results are presented as a series of Freundlich plots (log CO_2 concentration versus log weight of CO_2 adsorbed). Here it is seen that, with the exception of the 350°C. adsorption points, the data fall on or very close to straight parallel lines. Freundlich plots are typical of chemisorption processes and thus would be expected for the system: $MgO + CO_2 \longrightarrow MgCO_3$. The discrepancy shown by the 350°C. isotherm is probably due to the fact that magnesium carbonate decomposes appreciably at temperatures above 300°C.

Figure 19 is a conventional isosteric plot of the same data showing log of carbon dioxide concentration versus reciprocal absolute temperature for various amounts of carbon dioxide adsorbed. The two discordant points (on the left side) were taken from the 325°C. isotherm which, even though it is a straight line, was probably affected by the vapor pressure of magnesium carbonate. The fact that the isosteres have the same slope (same isosteric heats for different amounts adsorbed) is characteristic of a system in which a well-defined adsorbent-adsorbate complex is formed, of definite bond energy.

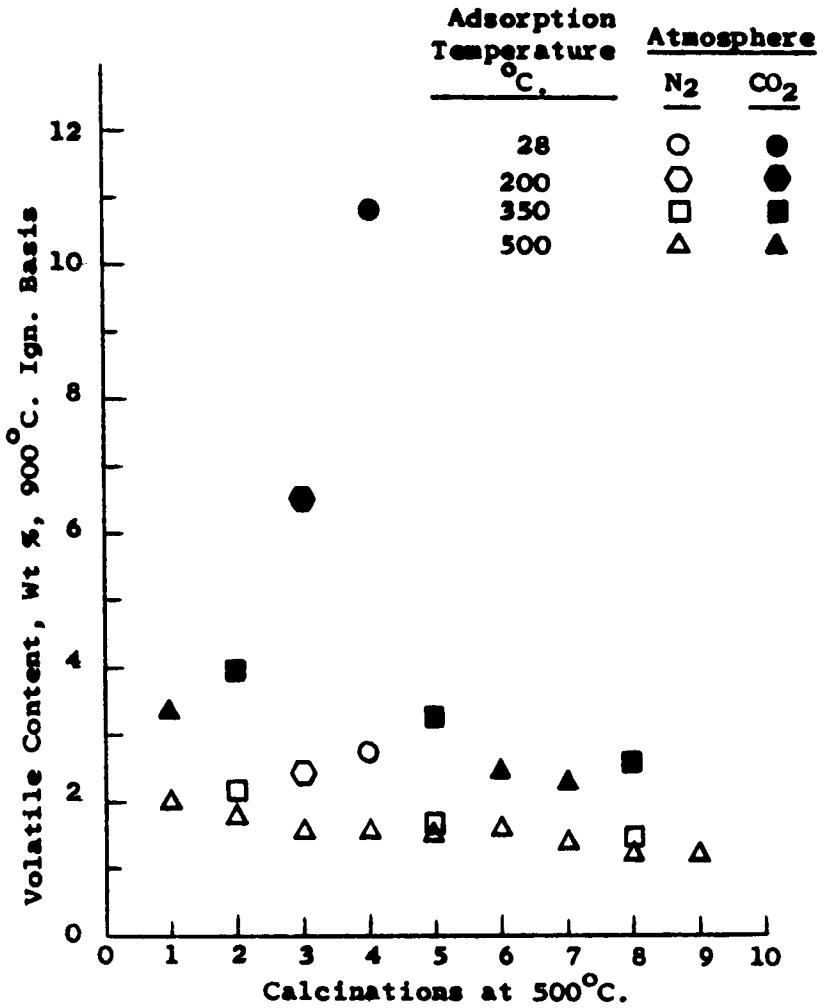


FIGURE 17 EFFECT OF REPEATED 500°C. CALCINATIONS ON EQUILIBRIUM ADSORPTION OF CARBON DIOXIDE BY MAGNESIA

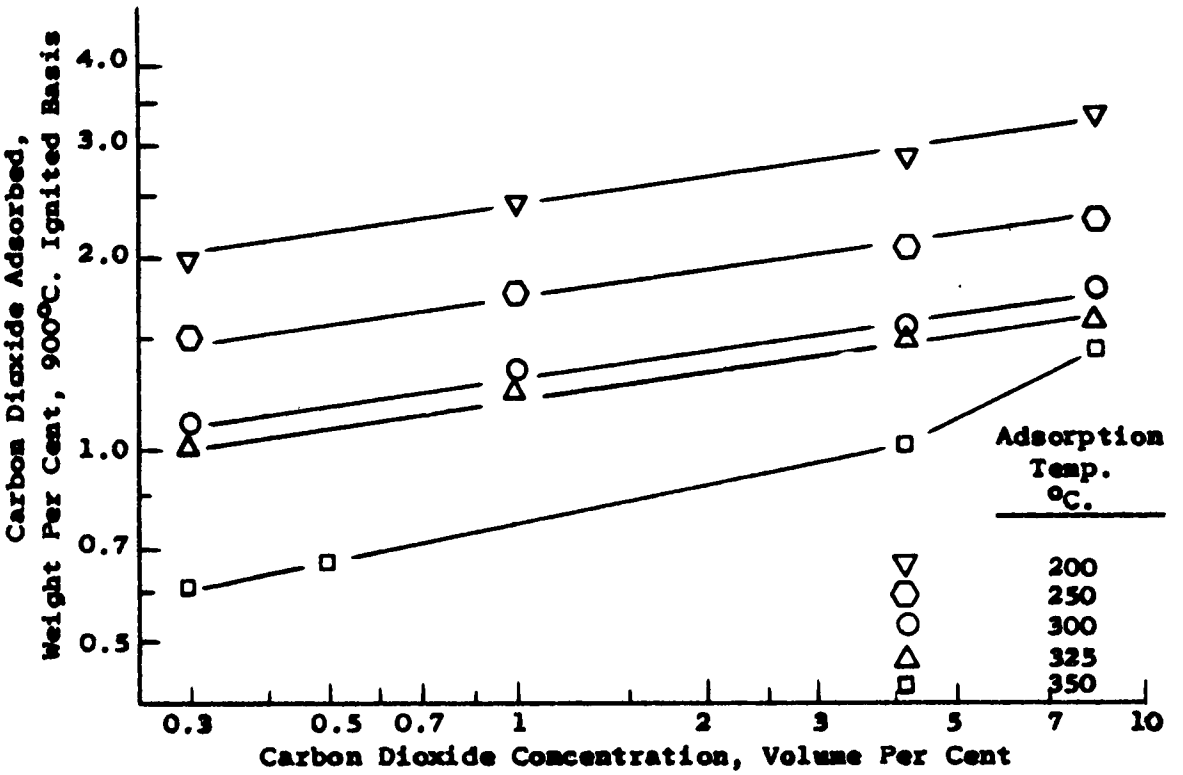


FIGURE 18 CARBON DIOXIDE ISOTHERMS FOR MAGNESIA CALCINED AT 400°C.

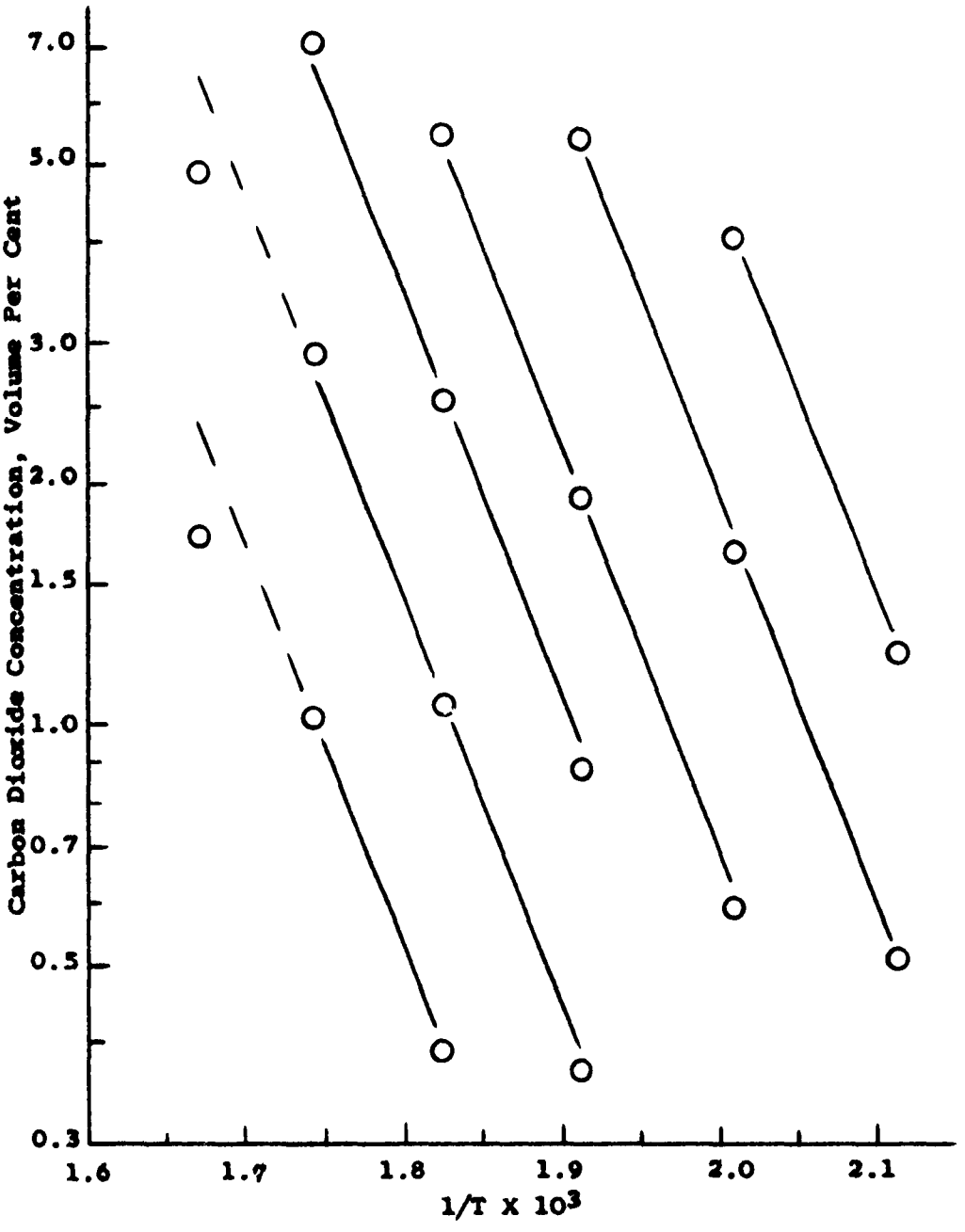


FIGURE 19 CARBON DIOXIDE ISOSTERES FOR MAGNESIA CALCINED AT 400°C.

In this instance the isosteric heat of adsorption of carbon dioxide by magnesia, calculated in the usual way with the Clausius-Clapeyron equation, was found to be 23.1 kcal/mole. This agrees well with the work of Marc and Simek[4] who reported -23.2 kcal/mole for the heat of dissociation of magnesium carbonate.

APPENDIX II

ANALYSIS OF ISOTOPICALLY ENRICHED WATER

J. H. Terrell

Water enriched with O^{18} can be analyzed by equilibrating the sample with CO_2 and analyzing the enriched carbon dioxide by means of the mass spectrometer.[5] This indirect approach has been favored because of the strong adsorption of water in the mass spectrometer.[6] Obvious disadvantages with the equilibration technique are the lengthy equilibration time and the extreme care necessary for handling and measuring the reactants. If the adsorption effect within the mass spectrometer can be eliminated or minimized, the direct approach offers better accuracy and less analytical time.

Techniques previously reported[7] with alcohols suggest that pretreatment of the mass spectrometer inlet system with the sample to be analyzed can reduce the effects of adsorption. A similar approach was tried with isotopically enriched water, and the experimental data indicate that the surfaces of the inlet system can be equilibrated in a reasonable length of time. However, it is equally important that a fixed schedule of sample residence time and pump-out time be maintained.

Deuterium Enrichment

While no noticeable exchange of O^{18} and O^{16} occurs during the adsorption process, there can be shown to be considerable exchange[8] of hydrogen and deuterium. Figure 20 illustrates the production of HDO^{16} and HDO^{18} as a result of hydrogen and deuterium exchange when a sample containing D_2O^{16} is admitted to the mass spectrometer. Because of mass interference at the H_2O^{18} ion peak, it is not possible to analyze the resultant mixture. A complete O^{18} balance must be computed from the sum of mono-ions at m/e H_2O^{18}, HDO^{18}, and D_2O^{18}. The following table illustrates the mass effect of deuterium oxide:

m/e	Ion Structure
17	HO^{16}
18	H_2O^{16}, DO^{16}, O^{18}
19	HDO^{16}, HO^{18}
20	D_2O^{16}, H_2O^{18}
21	HDO^{18}
22	D_2O^{18}

The spectrum is further complicated if there are appreciable quantities of O^{17} present. The adsorbed deuterium oxide can be removed from the inlet system by treatment with water as shown in Figure 21.

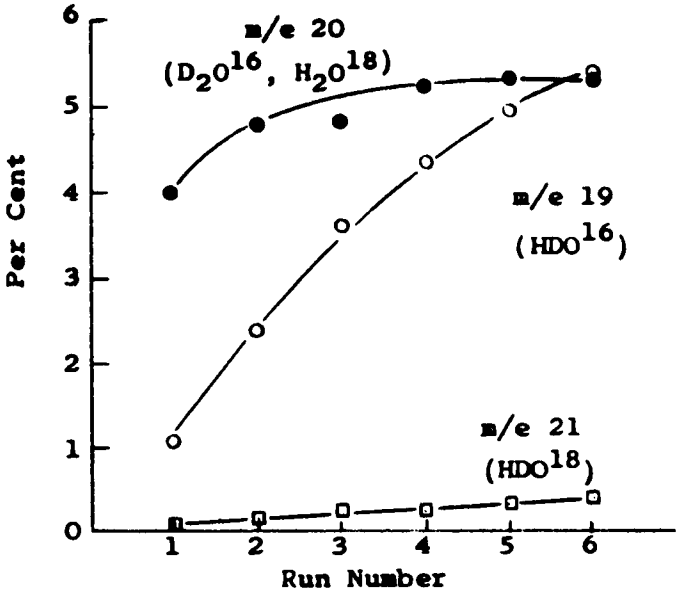


FIGURE 20 HYDROGEN DEUTERIUM EXCHANGE

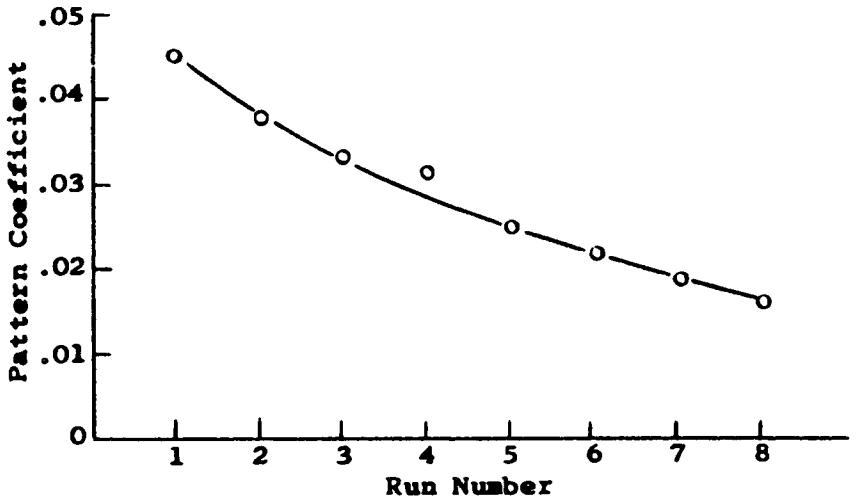


FIGURE 21 EFFECT OF H_2O EQUILIBRATION WITH ADSORBED HDO^{16}

Calibration

Normally, spectra of all the $H_2O^{(x)}$ species should be obtained with the mass spectrometer for calculation purposes. However, since pure H_2O^{18} has not been available for this purpose, some inferences have been made with regard to its spectral pattern and ion sensitivities. Previous work with isotopically enriched compounds indicated that fragmentation is similar to that obtained with the normal compounds. Small differences in bond cleavage, however, have been noted. Total ionization and parent ion sensitivities, which depend primarily on ionization potential and size of the molecule, do not differ by any appreciable amount. For all practical purposes, the following estimated pattern for H_2O^{18} has been found acceptable. Minimum residuals observed at m/e 19 in the sample spectra confirm these estimates.

m/e	H_2O^{16}	H_2O^{18}
16	.0361	
17	.2813	
18	1.0000	.0361
19	.0022	.2813
20	.0023	1.0000

Because the residuals observed at m/e 19 in the sample spectra are generally less than 2 per cent of the calculated H_2O^{18}, it can be assumed that, on the basis of equal total ionization for both species (H_2O^{16} and H_2O^{18}), the parent ion sensitivities are essentially the same.

Analytical Procedure

The following analytical procedure has been found acceptable for samples containing 1.5 per cent O^{18} or less. It is reasonable to assume that samples containing more than this amount of O^{18} can be successfully analyzed by extending the number of runs required to reach equilibrium within the mass spectrometer inlet system.

1. Introduce normal water to the mass spectrometer system and record its mass spectrum. If the ratio of m/e 19 and m/e 20 to m/e 18 exceeds the normal abundance ratio by more than 0.0005, repeat the introduction and scanning until it is acceptable.

2. After each scan of the spectrum is completed, pump on the expansion volume and leak line for five minutes. Seal the expansion volume from the vacuum system and pump on the inlet lines for five minutes. (Do not reduce or exceed these pump-out times.)

3. Analyze in a similar manner the charge stock which is being used for the isotopic exchange studies. Repeat the introduction and record the spectrum a total of four times. After each run, maintain a constant pump-out time as noted in step 2.

4. Introduce the H_2O^{18} samples and analyze with four repeated runs as noted in step 3.

5. Analyze all H_2O^{18} samples without interruption of the mass spectrometer for other types of analyses. If the sequence must be interrupted, start at step 1 again before continuing with the H_2O^{18} samples.

6. If the series of samples cannot be completed in a single shift operation, do not pump on the bottle or inlet system overnight. Continue with the analysis the following day as if there had been no interruption of activity.

Note: It is important that a consistent operational schedule be maintained at all times.

Sampling

It is preferable that the H_2O^{18} samples be submitted for analysis in the liquid phase, either in ampoules or sealed capillary tubes. Introduction to the inlet system of the mass spectrometer is accomplished by sampling with a capillary dipper and admitting the sample to the inlet through a mercury orifice system. Samples may be withdrawn from the capillary tubes by means of a micro-syringe and then injected into the micro-pipet. The size of the sample introduced should be such that the peak height on the spectral chart gives greatest accuracy for measuring both the m/e 18 and m/e 20.

Calculations

The amount of H_2O^{18} is computed directly from the ion intensity at m/e 20 without correction for the isotopic abundance of normal water. If argon exists in the mass spectrometer as background material (a normal situation for ionization pumps), its spectral contribution to m/e 20 must be deducted. Per cent H_2O^{18} is then computed as:

$$\frac{\Delta \text{ m/e } 20}{\Delta \text{m/e } 20 + \text{m/e } 18} \times 100$$

Discussion

Isotopic O^{18} water samples may be analyzed successfully if the following precautions are observed:

a. Charge stock and samples must be free of deuterium oxide in excess of its natural abundance.

b. Inlet system (including expansion chamber and leak line) must be thoroughly equilibrated with the sample to be analyzed.

c. Consistent pump-out times must be maintained. All operations must be on a fixed schedule.

d. Samples must be analyzed as a group without interruption.

Precision

After proper equilibration, the repeatability of the determinations depends on instrument reproducibility and the accuracy of measuring the peak heights. Normally, a mass spectrometer will reproduce spectra to within less than one per cent relative. The accuracy of measuring the peak height is about ± 0.02 per cent absolute between the range of 0-5 per cent H_2O^{18}. Above the 5 per cent level, range multiplying factors increase the absolute error to ± 0.06 per cent absolute. At the level of 1.5 per cent H_2O^{18}, deviation in data of ± 0.03 per cent can therefore be expected. Deviations greater than this for duplicate runs should be attributed to incomplete adsorption or uncontrolled equilibrium in the mass spectrometer inlet system.

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Aeronautical Systems Division, Dir/Materials and Processes, Metals & Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt No. ASD-TDR-62-843. AN INVESTIGATION OF PHYSICAL PARAMETERS OF NON-ELECTRICALLY CONDUCTING FINE PARTICULATES. Final report, Mar 63, 43pp. incl illus.,table, 8 refs.
Unclassified Report

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2. Sinterability
3. Magnesium oxide
I. AFSC Project 7350, Task 735001
II. Contract AF 33(616)-8032
III. Houdry Process and Chemical Co, Linwood, Pa.
IV. D. W. Koester, E. B. Cornelius, J. J. Donovan
V. Aval fr OTS
VI. In ASTIA collection

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